Electrokinetic phenomena in microstructures

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Electrokinetic Phenomena in Microstructures

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Abstract

Recent development in micro-fabrication technologies has enabled a variety of miniaturized fluidic systems consisting of micro-ducts, valves, pumps and various injection systems. With the rapid development of microfluidics in the past few years, electroosmosis has drawn a wide attention due to its fluid controlling ability. Hence many microfluidic devices use electrokinetic flow to transport, separate and mix samples. This thesis addresses the following three topics relevant to electrokinetic phenomena in microfluidic systems: (1) numerical investigation of electroosmotic flow mixing in a converging Y-shaped micromixer with various inlet bifurcation angles; (2) depth-averaged electrokinetic instability model for the dilute binary electrolyte with concentration gradient; (3) steady state and dynamic aspects of electroosmotic driven flow in the open-end and closed-end irregular shaped microchannels under the application of direct current (dc) and sinusoidally alternating current (ac) electric fields for micro-actuator applications.

Mixing is a crucial process in many microfluidic devices. Electrokinetic flow is an elegant method for flow control in microfluidic and nanofluidic systems since an electric field instead of moving parts, controls the flow. Though the Y-mixer is commonly used and constructed in micro-fluidics, the inlet bifurcation angle on the mixing efficiency within the mixing channel has not been reported. A finite volume, multi-block, body fitted numerical method is used to solve the coupled electric potential, Navier-Stokes and

Abstract

species transport equations. A variety of inlet bifurcation angles, electric field strengths, and channel sizes have been examined with the goal of the optimum design.

Moreover, electrolytes of interest may be nonhomogeneous; hence concentration mismatches often occur between the samples and the buffers solutions. Nonhomogeneous ionic concentration fields in the presence of applied electric field can, under certain conditions, generate an unstable flow field owing to electrokinetic instabilities (EKI). Electrokinetic instabilities can be leveraged for the rapid mixing. Linear stability analysis and numerical simulation model are developed to quantitatively describe the electrokinetic instability in micromixing. Using the linear stability analysis, the instability mechanism is explored through parametric study. To obtain a detailed time evolution of the instability, an unsteady 2-D numerical model is developed to investigate the non-linear behavior. The results show that the interface of adjacent electrolytes is strongly disturbed due to the high concentration gradient.

Lastly, in an attempt to develop an electrokinetic actuator using the concept of electroosmotic flow in closed-end packed capillaries, semi-analytical models for electroosmotic driven flow in open-end and closed-end irregular shaped microchannels are developed. The numerical model developed allows similar studies to be extended to any arbitrary cross-section. The results demonstrate that a higher frequency leads to the compression of the perturbed flow region. The induced pressure gradient increases with increasing the frequency of the applied electric field.

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Dedicated to my parents

to my husband, Lv Xin

and to my little baby, Jingyan

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Nomenclature

Nomenclature

Symbols

A	cross-section area of the specified geometry [m^2]
bn	the block that is to be executed
c	concentration of the interested species [M]
c_r	reference concentration of the interested species [M]
$\bar{c}_0$	species concentration in the completely unmixed (can be either 0 or 1)
$\bar{c}_\infty$	species concentration in the completely mixed states (= 0.5)
$c_r \equiv \omega_r / k$	phase velocity
D	diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
D_i	diffusion coefficient of the type- i ion [$\text{m}^2 \text{s}^{-1}$]
D_+, D_-	diffusion coefficients of the positive and negative species [$\text{m}^2 \text{s}^{-1}$]
D_{eq}	effective diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
D_h	hydraulic diameter of the microchannel [m]
e	elementary charge, 1.602×10^{-19} [C]
E_0	applied electric field [KV cm^{-1}]
EV_{EO}	ratio of electroviscous velocity to electroosmotic velocity
$\vec{F}$	force [N]
F	Faraday's constant, 96,485.34 [C mol^{-1}]
h	height of the microchannel [m]
$\vec{j}_i$	molar flux of the i th species
k_B	Boltzmann constant, 1.381×10^{-23} [J K^{-1}]
k	wave number
K	electrokinetic parameter
L_{arm}	length of the inlet channel [m]
L_{mix}	length of the mixing channel [m]
L_{diff}	diffusion length across the width of the micromixer [m]

Nomenclature

M	8×8 matrix operators [P. 77]
N	8×8 matrix operators [P. 76]
<i>nb</i>	the number of blocks
m_i	molar conductivity [$\text{Sm}^2\text{mol}^{-1}$]
Pe	Peclet number
$\frac{dP}{dz}$	pressure gradient in z direction [Pa m^{-1}]
Q_{EOF}	flow rate of the electroosmotic flow
$Q_{Pressure}$	flow rate of the pressure driven flow
r_0	boundary point D at $(r_0, 0)$
r_β	boundary point A at $(r_\beta, 0)$
R	gas constant, $8.314472 \text{ [J K}^{-1} \text{ mol}^{-1}]$
Re	Reynolds number
S	source term for Eq. (2.10)
T	temperature [K]
$\mathbf{T}^M$	Maxwell's stress tensor [Eq.(3.3)]
<i>u</i>	fluid velocity component in z flow direction [m s^{-1}]
u_ξ	velocity along ξ direction [m s^{-1}]
u_η	velocity along η direction [m s^{-1}]
$\vec{V}$	velocity vector
V_{ref}	reference velocity [m s^{-1}]
V_{EV}	electroviscous velocity scale $V_{EV} = \frac{\varepsilon E_0^2 w}{\mu}$
V_{EO}	<i>Helmholtz-Smoluchowski</i> velocity $V_{EO} = \frac{\varepsilon E_0 \zeta_0}{\mu}$
<i>w</i>	width of the microchannel [m]
<i>x</i>	local x coordinate
<i>y</i>	local y coordinate
$\bar{x}_a$	dimensionless coordinate parallel to the wall

Nomenclature

z_v	valence of the ions
z_+, z_-	valence number of positive and negative species

Greek Symbols

α	bifurcation angle α , of the Y-shaped channel
κ	<i>Debye – Hückel</i> parameter [m^{-1}]
ϕ	electric potential [V]
$\phi_{\max}, \phi_{\min}$	maximum externally applied electric potential and minimum externally applied electric potential [V]
φ	applied electric potential [V]
ψ	induced electric potential in the EDL [V]
ϵ_0	permittivity of vacuum [$\text{C V}^{-1} \text{m}^{-1}$]
ϵ_r	dielectric constant of the fluid
ρ_e	net electric charge density [C m^{-3}]
ζ	zeta potential [V]
λ_D	Debye length [m]
μ	dynamic viscosity of the fluid [$\text{kg m}^{-1} \text{s}^{-1}$]
β	angle between the two intersecting lines of symmetry
θ	angle of the boundary point
ρ	density of the fluid [kg m^{-3}]
Φ	general variable of the differential equation
ω	frequency of the applied electric field
ω_i	temporal growth rate
σ	electric conductivity [S m^{-1}]
η	mixing efficiency
γ	concentration ratio
δ	aspect ratio, $\delta = h / w$
$\bar{\omega}$	the ratio of the diffusion time scale to the period of the applied electric

Nomenclature

	field
Γ	diffusion coefficient

Subscript

n	previous iterative data
$n+1$	next iterative data
0	base state for disturbance equations
$\sim$	perturbation quantities
$—$	depth-averaged quantities

CHAPTER 1

Introduction

1.1 Background and Motivation

Recent development in micro-fabrication technologies has enabled a variety of miniaturized fluidic systems consisting of micro-ducts, valves, pumps and various injection systems. Microfluidic devices that perform various chip-based chemical and biological analyses have received significant attention over the past decade. Miniaturization offers key advantages including the following: higher throughput by way of parallelization; shorter analysis times; reduced sample volumes; and reduced operation and manufacturing costs (Kutter, 2000).

Mixing is a crucial process in many microfluidic devices such as micro Total Analysis Systems (μ TAS), Lab on a Chip, and micro-reactors which require that reagents can be added and samples diluted. However, mixing capability is hindered by very small scale of these microfluidic chips which tend to restrict the microchannel flows to laminar flow regime and hinder the use of conventional mixing mechanisms. Because of the low Reynolds number regime, species mixing is strongly diffusion dominated, as opposed to convection or turbulence dominated at higher Reynolds numbers. Consequently, mixing tends to be slow and occur over relatively long distances and time.

Chapter 1

In general, micromixers can be classified as active or passive. Passive micromixers do not require external energy; the mixing process relies entirely on diffusion or chaotic advection. Passive mixers can be categorized by the arrangement of the mixed phases: parallel lamination, serial lamination, injection, chaotic advection and droplet. Active micromixers use the disturbance generated by an external field for the mixing process. Active mixers can be further categorized by the types of external disturbance effects such as pressure, temperature, electrohydrodynamics, dielectrophoretics, electrokinetics, magnetohydrodynamics and acoustics. (Nguyen, 2005)

Because of the importance of mixing in microfluidic systems, numerous researchers have developed various mixing techniques. Electrokinetic flow is an elegant method for flow control in microfluidic and nanofluidic systems since an electric field instead of moving parts, controls the flow. Electrodes are easier to fabricate and incorporate into the miniature devices. Thus it can be used to transport liquid in micromixers as an alternative to pressure driven flow.

In principle, electroosmosis and electrophoresis are two kernel electrokinetic transport mechanisms used in the microfluidic devices. Electrophoresis refers to the migration of charged particles within an electrolyte solution relative to the fluid molecules under the influence of an applied electric field; while electroosmosis or electroosmotic flow (EOF) refers to a liquid flow induced by imposing an external electric field along an electrostatically charged capillary. Electroosmosis was first investigated by

Chapter 1

researchers in geophysical sciences, who found water migration through porous clay diaphragms under an applied electric field (Reuss, 1809). With the rapid development of microfluidic in the past few years, electroosmosis has drawn a wide attention due to its fluid controlling ability. Hence many microfluidic devices use electrokinetic phenomena to transport, separate and mix samples. It is essential to understand the characteristics of electrokinetic flow and its application on microscale mixing. We also know from Bejan (2000) that shape and structure spring from the struggle for better performance in both engineering and nature while being subject to global and local constraints. Different geometry configurations can influence the flow field, electric potential distribution and species mixing. After a broad review of the currently available literature on electroosmosis, it is noted that in many microfluidic devices mixing microchannels are constructed by integrating two or three inlet arms to the main channel in a “Y” configuration. Though the T-shaped mixer and Y-shaped mixer are commonly used, the influence of the inlet bifurcation angle on mixing efficiency has not been reported.

Moreover, electrolytes of interest may be inhomogeneous; hence concentration mismatches often occur between the samples and the buffers solutions. Inhomogeneous ionic concentration fields in the presence of applied electric field can, under certain conditions, generate an unstable flow field owing to electrokinetic instabilities (EKI). Electrokinetic instabilities can be leveraged for the rapid mixing. While good and fast mixing is required in microfluidic applications, effective

electrokinetic instability mixing scheme in microscale is still not well investigated.

Thus, this study serves as an attempt to fill the present void by carrying out a fundamental, systematic and in-depth exploration on the micromixing from the passive method “Y-shaped mixer” to the active method “electrokinetic instability” and on the transportation of electrolytes in irregularly shaped microchannels through electroosmosis.

1.2 Objectives and Scope

The objectives of the proposed project are:

- (1) To develop a numerical scheme for an electroosmotic driven flow in Y-shaped micromixers and to characterize the mixing efficiency.
- (2) To formulate the linear stability analysis and to develop a numerical scheme to investigate the mechanism of the electrokinetic instability.
- (3) To develop a semi-analytical scheme for an electroosmotic driven flow in irregularly shaped closed-end microchannels.
- (4) To model the dynamic responses of electroosmotic flow in both open-end and closed-end irregularly shaped microchannels under direct current (dc) and alternating current (ac) applied electric field.

Although most of this study is theoretical in nature, the information uncovered by the

Chapter 1

modeling results can be of great importance to the development and optimization of the electrokinetic micromixers or microactuator.

1.3 Outline of the Dissertation

There are five chapters in this thesis. Chapter 1 serves as an introduction to the background and motivation of this work. The latest development and application of microfluidics, the importance of micromixing and micropumping are presented. The objectives of the study are outlined.

Chapter 2 presents a numerical investigation of electroosmotic driven flow mixing in a converging Y-shaped micromixer with various inlet bifurcation angles. A finite volume, multi-block, body fitted numerical method is used to solve the coupled electric potential, Navier-Stokes and species transport equations. A variety of inlet bifurcation angles, electric field strengths, and channel sizes is examined with the goal of the optimum design.

In chapter 3, the linear stability analysis is performed to determine the critical electric field for the electrokinetic instability. The mechanism of electrokinetic instability is investigated in detail. Numerical scheme is presented for the electrokinetic instability mixing which captures the nature of the electrokinetic instability by coupling the electric field, flow fields and concentration field. Time evolutions of the instability are presented.

Chapter 4 presents a semi-analytical solution of steady state electroosmotic driven flow in open-end and closed-end four-point-star microchannels. Solutions for the irregularly shaped microchannels are presented. A numerical model is developed to investigate the unsteady electroosmotic flow in the four-point-star microchannels. The dynamic response and induced pressure gradient in a closed-end microchannel under the application of the direct current (dc) and sinusoidally alternating current (ac) electric field are presented. In chapter 5, results and findings are summarized and the future work is briefly outlined.

1.4 Literature Review

1.4.1 Electric Double Layer

Most surfaces acquire electric charges when they come in contact with a polar medium via ionization or ion adsorption or ion dissolution. For example, a glass surface immersed in an aqueous solution undergoes a chemical reaction in which fraction of the surface silanol group Si-OH is changed to Si-O⁻ or Si-OH₂⁺, resulting in a net negative or positive surface potential depending on the pH of the solution. This influences distribution of the ions in the buffer solution, as shown in Fig 1.1. The ions of the opposite charge (counterions) cluster immediately near the wall forming the Stern layer, a layer of typical thickness of one ionic diameter. The Stern layer is also known as the stagnant layer or compact layer. This layer behaves like a two dimensional gel where the ions and molecules of gel have mobility, but

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macroscopically it behaves like rigid solid as recently shown by the molecular dynamics studies (Lyklema *et al.*, 1998). The ions within the Stern layer are attracted to wall by very strong electrostatic forces.

Immediately after the Stern layer, thermal movement of ions takes an active role and forms the Gouy (diffuse) layer that contains both coions and counterions as shown in Fig 1.1. The plane separating the Stern layer and the diffuse layer is known as the shear plane. The shear plane (slipping plane) is an imaginary surface separating the thin layer of liquid bounded to the solid surface and the rest of liquid. Liquid between the wall and slip plane shows elastic behavior, where as the rest of the liquid shows viscous behavior. The electric potential at the shear plane is called zeta potential.

Zeta potential depends on salt or electrolyte concentration, surfactant concentration and pH of the solution, as shown in Fig 1.2. Normally strongest electrolytes create lower zeta potential than weaker electrolytes. The value of zeta potential is often the key to understanding dispersion and aggregation processes in applications as diverse as water purification, ceramic slip casting and the formulation of paints inks and cosmetics. Zeta potential can also be a controlling parameter in processes such as adhesion, surface coating, filtration, lubrication and corrosion. The interaction of particles in polar liquids is not governed by the electrical potential at the surface of the particle, but by the effective potential of the particle and its associated ions. Therefore, to utilize electrostatic control, it is the zeta potential of a particle that we

require to know rather than its surface charge (Hunter, 1981).

Figure 1.1 (A) Representation of the surface of fused silica tubing. (B) Formation of an electrical double layer near the surface of fused silica tubing (Remcho and Vallano, 2001)

The electric double layer (EDL) consists of both Stern layer and Gouy layer where ions are distributed diffusely. In electric double layer the number of counterions is more than that of coions. Hence the electric double layer itself is not electrically neutral, but the entire system as a whole is neutral and is governed by the following (Lyklema et al., 1998):

$$\sigma_o + \sigma_s + \sigma_d = 0 \tag{1.1}$$

where $\sigma_o, \sigma_s, \sigma_d$ are charge density at surface, Stern layer and Gouy layer, respectively. There are many concepts pertaining to the extent of the electric double layer. For example, Probst (Probst, 1994) thinks the edge of electric double layer is at where the electrical potential energy is approximately equal to the thermal

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energy of the counterions. On the other hand, Hunter (Hunter, 1981) extends the electric double layer where the electric potential reaches to zero.

Figure 1.2 Zeta potential of goethite (FeO (OH)) as a function of pH (Hunter, 1981)

1.4.2 Electroosmotic Flow in Microchannels

According to Pamukcu (1997), the electrokinetic phenomenon was first observed by Reuss in 1809. When a dc electric field was applied to a clay-water mixture, water moved through the capillary towards the cathode under the electric field. When the electric potential was removed, the flow of water immediately stopped. Helmholtz first treated electroosmotic phenomena analytically in 1879. The basic model for electroosmosis is attributed to Smoluchowski in 1921 on the consequences of applying pressure and potential gradients across capillaries filled with an electrolyte and developed the well-known Helmholtz-Smoluchowski (H-S) theory (Hiemenz, 1986). The H-S theory deals with electroosmotic and electrophoretic velocities of a

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fluid of certain viscosity and dielectric constant through a surface-charged porous medium of zeta potential (ζ) under an electric potential gradient. The formulation of the problem is based on the assumption of large electrokinetic diameter and the contribution due to the EDL thickness is neglected.

Burgreen and Nakache (1964) presented an analysis of mixed electroosmotically and pressure driven channel flow for very thin two-dimensional channels. They obtained analytical solutions for electroosmotic velocity and streaming potential in terms of elliptic integrals. Rice and Whitehead (1965) presented a theoretical study on cylindrical capillary without making any assumptions on the electrokinetic radius. They used the *Debye-Hückel* approximation to solve the Poisson-Boltzmann (P-B) equation. They also derived analytical expressions for electroosmotic velocity and streaming potential in terms of Bessel functions and discussed the electroviscous effects as an explanation of increased viscosity next to the wall.

Levine *et al.* (1975) extended the Rice and Whitehead model to high zeta potentials for the electrokinetic flow in cylindrical capillaries. They developed an analytical approximation to solve the P-B equation within the capillary, in a fashion similar to the method used by Philip and Wooding (1970) who solved this equation outside a charged cylindrical particle immersed in an electrolyte.

Ohshima and Kondo (1990) provided a theory for electroosmotic flow between two parallel plates with a surface charge layer and presented approximate relations for

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electroosmotic velocity, current and streaming potential. Dose and Guiochon (1993) presented a simulation for impulsively started electroosmotic flow. Lo and Chan (1994) prescribed the proper boundary conditions for electroneutrality of the system in solving the P-B equation.

Keh and Liu (1995) analytically studied the steady electroosmotic flow (EOF) in a long uniform circular capillary bearing a solvent-permeable and ion-penetrable layer of adsorbed poly-electrolytes on its inside wall. They obtained the electrical potential and space charge density distributions by solving the linearized P-B equation. Their results demonstrate that the structure of the surface charge layer can result in an augmented or diminished EOF relative to that in a capillary with bear walls, depending on the characteristics of the electrolyte solution, surface charge layer and capillary.

Söderman and Jönsson (1996) analyzed the electroosmotic flow induced by pulsed electric field. They analyzed both cylindrical and planner geometries for electric pulses in the same and opposite directions of flow. Mala *et al.* (1997) identified electrokinetic effects as one the main reasons for the deviation and provided a theoretical model based on the streaming potential.

The electrokinetic flow in rectangular microchannels has been studied by Yang *et al.* (1997, 1998, 2002a, 2002b). In these works, both steady state and transient, fully

developed, laminar liquid flow in rectangular microchannels were studied. The two-dimensional nonlinear P-B equation governing the electric double layer (EDL) was numerically solved using a finite difference scheme. An exact solution for the velocity of EOF was obtained by solving the modified N-S equation using the Green function method. The bulk temperature distributions were also achieved by solving the energy equation for a rectangular microchannel using the control volume method.

Qu and Li (2000) proposed a model to determine the electrical potential and ionic concentration distributions in an overlapped EDL fields. Two infinitely large plates were considered. It was found that using the classical theory to evaluate the potential distributions in an overlapped EDL region would lead to an inaccurate description due to the misuse of the Boltzmann equation and the boundary conditions. Hence they derived a new set of governing equations for the overlapped EDL fields without using the Boltzmann equation.

Tsao (2000) studied the electroosmosis flow through an annulus under the Debye-Hückel linear approximation. He introduced a geometry-dependent correction factor to the electroosmotic mobility described by the Helmholtz–Smoluchowski equation. Kang *et al.* (2002a) extended Tsao's model to study the electroosmotic flow in a capillary annulus with high zeta potential.

Ren and Li (2001) and Gleeson (2001, 2002) investigated the characteristics of the

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EOF in a cylindrical microchannel with a non-uniform zeta potential. Their theoretical and numerical results showed the distorted electroosmotic velocity profiles resulting from the axial variation of the zeta potential. The influences of the unequal section size and the direction of the zeta potential on the velocity profile, the induced pressure distributions, and the volumetric flow rate were discussed. The simulation results reveal possible effects of bio-adhesion in microchannels on the electroosmotic flow in biochip devices. Santiago (2001) extended the work for mixed EOF and pressure driven flows in two-dimensional microchannels for finite inertial and pressure effects. Hsu *et al.* (2002) studied the electrokinetic flow of an electrolyte solution through an elliptical microchannel theoretically.

The effects of electrostatic boundary conditions in molecular simulation to determine the interfacial properties are presented by Spohr (1997). This study shows that the atom density profiles, charge densities, dipole densities, free energy and force profiles are not very sensitive to the boundary conditions due to statistical error especially at large separation distances. Spohr (1999) modeled the electric double layer with interaction site models for NaCl solution in contact with a metallic surface. They used both charged and uncharged metallic surfaces, and suggested a longer simulation time to obtain reasonably converged ionic distribution. Lyklema *et al.* (1998) applied molecular dynamics method to simulate the ion distribution near the charged surfaces. The molecular interactions were modeled by the Lennard-Jones potential. Interactions of the wall, solvent and solute molecules in six different combinations

were modeled with different Leonard-Jones coefficients. The results confirm the presence of a stagnant layer of fluid very near the surfaces due to the interaction of fluid ions with the oppositely charged surface.

Numerical simulations of micro-fluidic injection using electroosmotic forced through intersection of two channels were presented by Patankar and Howard (1998) by using the *Debye – Hückel* linearization. They applied control volume algorithm to model the P-B and momentum equations. The numerical results show inertia dependence, especially for higher Reynolds number flows. Bianchi *et al.* (2000) used finite element formulation to model the electroosmotic flow through a T-channel junction. The numerical results show that pressure effects play an effective role. Lately they presented electroosmotic flow experiments on composite microchannels made of polyethylene terephthalate and reported the effect of zeta potentials due to composite structures on Taylor dispersion.

Söderman and Jönsson (1996) developed a theoretical framework for the description of time and spatial resolutions of electroosmosis for both planar and cylindrical geometries under the effect of pulsed electric fields. López-García *et al.* (2000) studied the dynamics of EDL in both time and frequency domains. They used a network method to obtain the evolution of the potential, ion concentration profiles, particle velocity and fluid velocity in the nanosecond to microsecond time range after the applied electric field. Griffiths and Nilson (2000) obtained the analytical solutions

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for the time-dependent neutral solute dispersion by solving the transient diffusion-convection equation in transformed spatial and temporal coordinates for both low and high zeta potentials.

Without assumption of thin double layer thickness, Keh and Tseng (2001) analytically studied the transient response of electrolyte solutions in a narrow capillary tube and slit to a step change in the applied electric field and pressure gradient by solving the linearized P-B equation. The modified Navier-Stokes equations were solved analytically to obtain the electrical potential and transient velocity profiles. Their results demonstrate that the behavior of the transient electrokinetic flow in a capillary tube and a capillary slit is similar; however, the rate of evolution of the flow in a tube with time is faster by a factor of about 2 than that in a slit with its half thickness equal to the tube radius.

Kang *et al.* (2002b) presented an analysis of the dynamics of electroosmotic flow in a cylindrical microcapillary. A time-dependent electric field was applied to the transient electroosmotic flow field. The flow field excited by a sinusoidal alternating current electric field was also discussed. The complete P-B equation and exact solutions for the transient velocity distributions were obtained using the Green's function formulation. In addition, Marcos *et al.* (2004) presented an analysis of the frequency and time-dependent electroosmotic flow in a closed-end rectangular microchannel.

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Yang *et al.* (2001a) investigated the time and space development for the entry region of an electroosmotic flow through a microchannel between two parallel plates by numerically solving the combination of the Poisson, Nernst-Planck, and Navier-Stokes equations. They discussed the effects of the entrance region on the fluid velocity distributions, charge density boundary layer, entrance length, and shear stress. They found that the entrance length of the electroosmotic flow is longer than that of the classical pressure-driven flow. The thickness of the electrical double layer (EDL) in the entry region is thinner than that in the fully developed region. The velocity profile across the channel height is in a parabolic shape at the entry point, and changes to a flat shape stage by stage as it moves to the fully developed region when the Reynolds number is small. The velocity profile will change to a concave shape in the fully developed region when the Reynolds number is large.

Lorente *et al.* (2007) used two different kinds of experiments to calculate the diffusion coefficient through the porous media. In the first, the porous medium sample was subjected to a concentration gradient, while in the second an electric field was applied. It was shown that in natural diffusion the chloride diffusion coefficient does not depend on the chloride concentration level and the concentration gradient. In the case of chloride-free samples, the existence of the competition between the two driving forces, namely, diffusion and electrical effects, was highlighted. It was also demonstrated that when the metrology of the experiments is carefully controlled, the flux of chloride is

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directly proportional to the external electric field. This leads to the result that the diffusion coefficient of an ionic species through a porous medium has a unique value.

Lorente (2007) applied the constructal law to the study of the ionic transfer through porous media under electric fields in two ways: (1) in time and (2) in space. The transport of ions is the result of two different mechanisms: diffusion and electrical effects. Constructal theory explains how the combination of the two mechanisms leads to an optimization of transport in time. The optimal location of the electrodes is also determined from the constructal law by setting the diffusive ionic flow rate equal to the ionic flow rate due to electrical effects.

1.4.3 Electroosmotic Flow in T-shaped and Y-shaped micromixers

Einstein's theory on thermal motion of molecules is the foundation for diffusion theory. In macroscale, the two common mixing methods are the generation of turbulence and chaotic advection. In a turbulent flow, fluid motions vary irregularly so that quantities such as velocity and pressure show a random variation in time and space. The random movement disperses the mixed components quickly. Chaotic advection can be generated by stirring the flow, which is effective for small Reynolds numbers. In macroscale, chaotic flow can be produced easily through stirring or heating. But in microscale, the Reynolds numbers are very small, so diffusion is dominant in the microfluidic mixing and turbulence is not available to enhance mixing. Furthermore, it is often not feasible to incorporate moving components, such as

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stirrers into micro devices. Thus, new approaches are needed. Electrokinetic flow is an elegant method for flow control in microfluidic and nanofluidic systems since an electric field instead of moving parts, controls the flow. Electrodes are easier to fabricate and incorporate into the miniature devices. Thus it can be used to transport liquid in micromixers as an alternative to pressure driven flow.

According to Fick's Law, mixing is based on diffusion whose flux f is described as:

$$f = -D \frac{\partial c}{\partial x} \quad (1.2)$$

where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) and c is the specie concentration (kg/m^3). The mixing time t is related to the width of the mixing path L :

$$t = \frac{L^2}{D} \quad (1.3)$$

which usually gives us a method to estimate diffusion distance. But recently, Ismagilov *et al.* (2000), Kamholz and Yager (2002) found this equation was not correct near the wall of the channel due to nonuniform velocity distribution. Song *et al.* (2003) did the similar attempt on the scaling law through experimental methods. They drew a conclusion from their experiments, the equation for the latter situation is

$$L = \sqrt[3]{2Dt} \quad (1.4)$$

Electrokinetic flow can be used to transport liquid in micromixers as an alternative to pressure driven flow. A numerical algorithm for electroosmotic and electrophoretic

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transport and species diffusion has also been developed by Ermakov *et al.* (1998) for a two-dimensional flow conduit. They considered two basic chip elements: channel crossing for sample focusing and injection, and T-shaped channel for sample mixing. Numerical results were compared with existing experimental data to validate the model. Jacobson *et al.* (1999) reported electrokinetically driven mixing in a conventional T-shaped mixer.

Bejan (2000) takes a close look at the derivation of geometric from constructal principle -the struggle for meeting the objective of better performance while being subject to global and local constraints. Such an examination of the purposeful and constrained optimization of engineering enables us to make better sense of nature's architecture. In the mean time, the design and optimization of man-made systems is generated from the natural systems by the constructal law. Bejan (2006) also mentioned that the structure and shape can influence the heat conduction, fluid flow and mixing.

Lettieri *et al.* (2001) proposed the use of the electrokinetic effect to disturb the pressure-driven flow in a micromixer. He *et al.* (2001) applied the serial lamination micromixer concept to the electroosmotic flows. Mixing is clearly enhanced using electroosmotic flows between the multiple intersection microchannels.

Tang *et al.* (2002) utilized an electrokinetic flow to improve mixing. Similar to the

previous pressure-driven approach, switching on or off the voltage supplied to the flow generates fluid segments in the mixing channel. This flow modulation scheme was capable of injecting reproducible and stable fluid segments into microchannels at a frequency between 0.01Hz and 1Hz.

Erickson and Li (2002) studied the effects of surface electrokinetic heterogeneity on the electroosmotic flow and mixing efficiency of a T-shaped micromixer through 3D numerical simulations. While all cases of surface heterogeneity were shown to enhance species mixing, they found that the greatest improvements can be achieved when the zeta potential of the heterogeneous surface is of opposite sign to that of the homogeneous surface, resulting in localized circulation zones within the bulk flow field.

Mengeaud *et al.* (2002) used a finite element model to study the mixing process of species in a 100- μm -wide zigzag microchannel integrating a “Y” inlet junction. The results demonstrated that the mixing is entirely molecular diffusion below a critical Reynolds number of 80. For higher Reynolds numbers, simulations revealed the mixing contribution of laminar flow recirculations. Experimental results on the mixing of species at different flow rates show the same hydrodynamic tendency.

Truesdell *et al.* (2003) combined two pulsatile fluid streams at a Y-connection. A peristaltic pump provided the mean flow with the action of two pinch valves, one on

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each arm of the Y-connection to generate strong pulsations. The chaotic conditions were realized in the confluence region superimposed with the mean flow. The work demonstrated a low cost and efficient mixing device for low-Reynolds number is suitable for miniaturization.

Takhistov *et al.* (2003) found that the irrotational character of Ohmic electroosmotic flow is violated due to electric field leakage across sharp corners. They demonstrated experimentally and theoretically evidence of electrolyte depletion and vortex separation in electroosmotic flow around a junction between wide and narrow channels.

Lin *et al.* (2004) employed a computer simulation to predict the mixing efficiency for the conventional and novel pinched switching mode of a T-shaped micromixer. The simulation results showed that a mixing performance as high as 97% can be achieved within a mixing distance of 1mm downstream from the T-junction when 60V/cm driving voltage and a 2-Hz switching frequency are applied in the pinched operation mode. Their study demonstrates how the driving voltage and switching frequency can be optimized to yield an enhanced mixing performance.

Chang and Yang (2004) presented a numerical investigation of electrokinetically driven flow mixing in microchannels with various numbers of incorporated patterned rectangular blocks. Furthermore, a novel approach was introduced which patterned

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heterogeneous surface on the upper faces of the rectangular blocks in order to enhance species mixing. The simulation results demonstrated that the introduction of rectangular blocks within the mixing channel slightly enhances species mixing. However, a large number of blocks are required with a long mixing channel to obtain the complete mixing. The patterning heterogeneous upper surface is an effective means of enhancing mixing. Increasing the magnitude of the heterogeneous surface zeta potential enables a reduction in the mixing channel length.

Glasgow *et al.* (2004) conducted the numerical simulations using Fluent and experiments on the T-shaped micromixer. They demonstrated that good mixing is shown to occur when the electroosmotic flow at the two inlets pulse out of phase, the Strouhal number is on the order of 1 and pulse volumes are on the order of the intersection volume.

Lee *et al.* (2004) presented an electrokinetically driven active micro-mixer which used localized capacitance effects to induce zeta potential variations along the surface of silica-based microchannels. The potential variations induced flow velocity changes within a homogeneous fluid and a rapid mixing effect with the alternating electric field. The numerical and experimental results demonstrated that the developed microfluidic device permits a high degree of control over the fluid flow and an efficient mixing effect.

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Fu. *et al* (2005) utilized low-frequency periodic electrokinetic driving forces to mix electrolytic fluid samples in T-shaped micromixers and double-T- shaped micromixers. The simulation and experimental results confirmed that the double-T-form micromixer has excellent mixing capabilities. The mixing efficiency can be as high as 95% within a mixing length of 1000 μm downstream from the secondary T-junction when a 100V/cm driving electric field and 2 Hz switching frequency are applied.

Wu and Liu (2005) took advantage of field-effect control to manipulate local flow field to obtain a high mixing efficiency in a T-shaped micromixer. Theoretical analysis and numerical simulation including the influences of buffer pH, electrolyte concentration and radial voltage on the zeta potential and the flow field analysis with nonuniform zeta potential were reported. Experimental results indicated that over 90% mixing efficiency can be achieved for a 5 mm long microchannel. The velocity profile distortion resulting from the nonuniform zeta potential was also observed.

Colemann and Sinton (2005) presented a novel micromixing strategy which exploits the axial diffusion of a continuous sequence of discrete samples in a microchannel expansion. Mixing of a continuous sequence in an electroosmotic flow through a sudden expansion region was modeled assuming an ideal, square-wave injection. These results indicated that the effectiveness of this micromixing strategy is critically dependant on the injection method.

1.4.4 Electrokinetic Instability Phenomenon

Several reviews have focused on engineering challenges or the mechanics of dispersion and mixing (Ghosal, 2004; Locascio, 2004; Stone, Stroock and Ajdari 2004). Many of these microfluidic devices use electrokinetic phenomena to transport, separate and mix samples (Harrison, *et al.* 1992; Bruin, 2000). Electrokinetics is a branch of electrohydrodynamics (EHD) that describes the coupling of ion transport, fluid flow and electric fields. The fluid flow in this class of devices is often stable and strongly damped by viscous forces due to small Reynolds numbers. However, heterogeneous ionic conductivity fields in the presence of applied electric fields can, under certain conditions, generate an unstable flow field owing to electrokinetic instabilities (EKI). Electrokinetic instabilities can be leveraged for rapid mixing or can cause undesirable dispersion in sample injection, separation and stacking. These instabilities are caused by a coupling of electric fields and ionic conductivity gradients.

Melcher and Taylor (1969) observed EHD flow instabilities in so-called 'leaky-dielectric' liquids (such as corn oil) with electrical conductivity gradients and applied electric fields. Hoburg and Melcher (1977) observed that an electric potential applied transverse to a conductivity gradient in a flow cell created an interface of ionically doped and undoped corn oil. Their work showed the interaction of an applied field and conductivity gradients generates regions of net charge in the low conductivity liquid system. Baygents and Baldessari (1998) performed a linear

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stability analysis on a quiescent thin layer of liquid in which the electrical conductivity varies linearly over the depth of the layer. The conditions for marginal stability were determined; the analysis showed that the relevant dimensionless groups are the electric Rayleigh number, relative conductivity increment, the ratio of viscous to charge relaxation times and the transverse wave number of the disturbance.

Oddy *et al.* (2001) observed electrokinetic instabilities in microchannel structures and made use of these instabilities for rapid continuous flow micromixing using the alternating electric fields. Lin *et al.* (2004) analyzed the two dimensional linear stability analysis of the two-ion symmetric binary electrolyte (SBE) model and conducted nonlinear flow simulations. They showed that the model provides good qualitative and fair quantitative agreement with regard to the threshold electric field and critical wave number for a conductivity ratio 10. Story *et al.* (2005) developed a thin channel model for fluid flow and compared the model with a three dimensional model. They find good agreement between these models. Chen *et al.* (2005) demonstrated that electro-osmotic flow in electrokinetic systems leads to convective and absolute instability. When the internally generated electroviscous velocity disturbances are high enough to overcome electroosmotic convection, there is absolute instability. Both the electroviscous and electroosmotic velocities result from balancing electric body forces and viscous stresses. Oddy and Santiago (2005) considered a multiple species model that can be used to analyze either SBE or non-SBE systems. Posner and Santiago (2006) used quantitative epifluorescence

imaging to present the parametric experimental results of convective electrokinetic instability in an isotropically etched, cross-shaped microchannel.

In the experimental investigations, Shin *et al.* (2005) applied a time-periodic electric field to excite the instability in a cross channel. Through the frequency sweeping from 0.1 Hz to 50 Hz, they found that the instability is most enhanced when the period of the applied electric field is about half of the period of instability in the form of a sinusoidal wave generated under a the static electric field. Park *et al.* (2005) found that the mixing efficiency due to electrokinetic instability is increased by about 15% for the channel with herringbone-shape cavities as compared with the straight channel.

1.4.5 Electroosmotic Pumps

Pumping in microfluidic systems can be accomplished by using pressure or electric fields. The pressure building ability of electroosmosis made it very suitable as a pumping mechanism in microchannels for electronic cooling and bio-analytical systems. Most mechanical pumps make use of a membrane that can be activated piezoelectrically, pneumatically, electrostatically or electromagnetically. Although these membrane pumps offer several advantages, such as bidirectionality, constant flow rate and the ability to pump almost any kind of liquid phase with a typical range of 1-100 $\mu\text{l min}^{-1}$, their major inconvenience is related to the nature of the membrane actuation, which produces a pulse flow. At the sub-ml min^{-1} domain, peristaltic pumps

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can not operate reliably in this scale and their tubes must be frequently replaced in order to maintain constant flow rates. Additionally, the design and manufacture of micro-scale in the traditional materials such as silicon or glass is difficult. These devices require multiple levels of fabrication, and are easily damaged by particles of dust and contaminants in the fluid. Another disadvantage of mechanical pumps is associated with the velocity profile. Poiseuille flow in pressure driven motion, is characterized by a parabolic velocity profile across the capillary, presenting zero velocity at the walls and a maximum velocity at the center of the channel. In some applications, the flow is used to separate different molecules in a solution. Poiseuille flow spatially broadens the band of distinct species.

In electroosmotic flow, the velocity profile is basically flat over the cross section of the channel. This type of flow is ideal for separations based on the charge-to-size ratio of the molecular components of biological samples in solution, since broadening of the separated bands of differing species occurs only for diffusion, not as a result of the differences in flow velocity across the channel. In addition, electroosmotic flow is easier to control since the only driving force involved is the external applied electrical field.

Figure 1.3 Flow characteristics of different micro-pumps.

(Adopted from Microfluidics Lab, Stanford University, CA, USA.)

Fig 1.3 shows the pressure building ability of different micro-pumps. Electroosmotic pumps can generate pressures in excess of 10 and even 100 atm. Electroosmosis is a very promising technology for pumping liquid in micro-devices. Some of the works reported on electroosmotic micropumps are summarized below.

Zeng *et al.* (2001) developed electroosmotic micropumps which achieved pressures in excess of 20atm and flow rates of $3.6 \mu\text{l min}^{-1}$ for 2kV applied potentials. These pumps used deionized water as working fluids in order to reduce the ionic current of the pump during the operation and increase its thermodynamic efficiency. Electroosmotic micropumps are fabricated by packing the $3.5 \mu\text{m}$ diameter non-porous silica particles into 500-700 μm diameter fused-silica capillaries and by using a silicate frit fabrication process to hold the particles in place.

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Chen *et al.* (2002) fabricated a planar electroosmotic micropump. An analytical model applicable to planar, etched-structure micropumps was developed. The model consists of pressure and flow relations in addition to an analytical expression that can be used to estimate the thermodynamic efficiency of the planar electroosmotic pump. The working fluid was deionized water with a conductivity of 3.0×10^{-4} S/m (pH=5.7). The EO micro-pumps were fabricated on a soda-lime glass substrate using standard microlithography and chemical wet etching techniques. The pump can produce a maximum pressure of 0.33 atm and a maximum flow rate of $15 \mu\text{l min}^{-1}$ at 1kV.

Lazar *et al.* (2002) fabricated a novel, fully integrated, miniaturized pumping system for the generation of pressure driven flow in microfluidic platforms. The micropump has a multiple open channel configuration consisting of hundreds of parallel, small diameter microchannels. Pressures up to 80 psi and flow rates $10\text{-}400 \text{ nl min}^{-1}$ were produced.

Yao and Santiago (2003) presented an analytical study of electroosmotic pumps with porous pumping structures and developed an analytical model to calculate electroosmotic flow rate, pumping power, and thermodynamic efficiency as a function of pump pressure load for porous structure electroosmotic pumps. The model uses a symmetric electrolyte approximation which is valid for the high-zeta-potential regime. The authors also fabricated the sintered-glass electroosmotic pumps that provide maximum flow rates and pressure capacities of 33 ml min^{-1} and 1.3 atm, respectively,

at applied potential 100 V. These pumps were designed to be integrated with two-phase microchannel heat exchangers with the load capacities of order 100 W and greater. Experiments were conducted with pumps of various geometries and using a relevant, practical range of working electrolyte ionic concentration.

1.4.6 Summary

After a broad review of the currently available literature on electroosmosis in microchannels, it can be concluded in the following:

1. Electrokinetic flow is an elegant method for flow control in microfluidic and nanofluidic systems at low Reynolds number since an electric field instead of moving parts controls the flow. In addition, electrodes are easier to fabricate and incorporate into the miniature devices. Thus it can be used to transport liquid in micromixers as an alternative to pressure driven flow.
2. Most of the numerical works reported concerning electroosmotic flow in a relatively simple geometries such as the T-shaped channel and L-shaped channel. In many microfluidic devices, the mixing microchannels are constructed by integrating two or three inlet arms to the main channel in a “Y” configuration. Though the Y-mixer is commonly used and constructed in micro-fluidics, to our knowledge the influence of inlet branch geometry, i.e. the inlet bifurcation angle on the mixing efficiency within the mixing channel has not been reported.

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3. Electrolytes of interest may be Inhomogeneous; hence concentration mismatches often occur between the samples and the buffers solutions. Electrokinetic instabilities can be leveraged for the rapid mixing of the inhomogeneous electrolytes. From the published experimental observation (Chen *et al.*, 2005), it is noted that as the applied electric field strength above a critical value, the fluids concentration profiles exhibit complex wave structures, at higher applied electric field, the flow becomes chaotic. Hence it is essential to understand the complex flow characteristics and the mechanism of electrokinetic instability through a systematic parametric investigation of the flow variables and in-depth numerical simulation.
4. The literature survey shows that so far all the reported work focuses on the electroosmotic flow in regularly shaped microchannels. In an attempt to develop an electrokinetic actuator using the concept of electroosmotic flow in closed-end packed-capillaries, it is possible for fluid flow within or outside the packed-capillaries which means flow in star point microchannels. Furthermore, the comparison of the flow characteristics between regular and irregular geometries has not been reported.

CHAPTER 2

Electroosmotic mixing in Y-shaped micromixers

2.1 Introduction

Because of the importance of mixing in microfluidic systems, numerous researchers have developed various mixing techniques. Electrokinetic flow is an elegant method for flow control in microfluidic and nanofluidic systems since an electric field instead of moving parts, controls the flow. Electrodes are easier to fabricate and incorporate into the miniature devices. Thus it can be used to transport liquid in micromixers as an alternative to pressure driven flow.

The review shows that most of the numerical works reported concerning electroosmotic flow in a relatively simple geometries such as the T-shaped channel and L-shaped channel. In many microfluidic devices, the mixing microchannel are constructed by integrating two or three inlet arms to the main channel in a “Y” configuration as shown in Fig. 2.1. At the intersection of the two inlet laminar flows (Fig. 2.1), a mixing region is formed which extends and evolves downstream in the mixing channel. The mixing efficiency within the mixing channel depends on the fluid properties, the mixing channel length, the channel cross sectional dimensions and the inlet branch geometry. Though the Y-mixer is commonly used and constructed in micro-fluidics, to our knowledge the influence of inlet branch geometry, i.e. the

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inlet bifurcation angle on the mixing efficiency within the mixing channel has not been reported.

In this part of the thesis, the fundamental influence of bifurcation angle on the flow and species mixing in electroosmotically driven microfluidic devices, through the use of 2D body fitted coordinate multiblock flow simulations will be presented. A variety of bifurcation angles, electric field strengths, and channel sizes will be examined with the goal of determining the optimum conditions for enhanced mixing.

2.2 Mathematical Formulation

Fig. 2.1 shows the schematic of the problem considered. Two streams enter a Y-shaped microchannel through two inlets as a result of an applied electric potential at the two inlets and one outlet. These two streams interact to form a mixture of the two streams downstream from the inlet. The bifurcation angle α , of the Y-shaped channel is shown in Fig. 2.1.

Figure 2.1 Y-shaped micromixer formed by the intersection of two microchannels.

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2.2.1 Governing Equations

The “thin EDL” approach where the EDL velocity is specified at the walls is used in this analysis. As a result, the continuity and momentum equations for steady flow of an incompressible fluid are

$$\nabla \cdot \vec{V} = 0 \quad (2.1)$$

$$\rho(\vec{V} \cdot \nabla) \vec{V} = -\nabla P + \mu \nabla^2 \vec{V} \quad (2.2)$$

where $\vec{V}$ is the velocity vector, ρ is the density of the fluid and, μ is the dynamic viscosity of the fluid.

These dimensionless parameters are defined as

$$\begin{aligned} \bar{x} &= \frac{x}{w} & \bar{y} &= \frac{y}{w} & \bar{t} &= \frac{t}{\frac{w}{V_{ref}}} \\ \bar{P} &= \frac{P - P_{atm}}{\rho V_{ref}^2} & \bar{\vec{V}} &= \frac{\vec{V}}{V_{ref}} & Re &= \frac{\rho_f V_{ref} w}{\mu} \end{aligned} \quad (2.3)$$

where w and Re are the channel width, Reynolds number respectively. The variables with an overbar denote dimensionless quantities. The reference velocity is defined as

$$V_{ref} \equiv \frac{\varepsilon \zeta (\phi_{\max} - \phi_{\min})}{\mu (L_{arm} + L_{mix})} \quad (2.4)$$

where ε , ζ , L , $\phi_{\max}$, and $\phi_{\min}$ are the fluid permittivity, zeta potential, channel

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lengths (see Fig. 2.1), maximum externally applied electric potential and minimum externally applied electric potential respectively. The dimensionless applied electric potential $\bar{\phi}$ distribution is obtained by solving the conservation of electric charge; which for constant electric conductivity can be written as

$$\nabla^2 \bar{\phi} = 0 \quad (2.5)$$

where

$$\bar{\phi} \equiv \frac{\phi}{\phi_{\max} - \phi_{\min}} \quad (2.6)$$

The dimensionless concentration of the solution $\bar{c}$ is calculated via

$$\bar{\vec{V}} \cdot \nabla \bar{c} = \frac{1}{Pe} \nabla^2 \bar{c} \quad (2.7)$$

The dimensionless concentration and the Peclet number are defined as

$$\bar{c} = \frac{c}{c_r}, \quad Pe = \frac{V_{ref} w}{D} \quad (2.8)$$

where c_r and D are the reference concentration of the interested species in the buffer solution and the diffusion coefficient respectively.

2.2.2 Boundary Conditions

The local wall velocities are specified via the local applied electric field namely,

$$\bar{u}_{wall} = \frac{\varepsilon \zeta \left(\partial \bar{\phi} / \partial \bar{x}_a \right) (\phi_{\max} - \phi_{\min}) / w / \mu}{V_{ref}} \quad (2.9)$$

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where $\bar{x}_a$ is the dimensionless coordinate parallel to the wall. The inlet velocity tangential to the inlet is set to zero. The axial gradient of the inlet velocity normal to the inlet is set to zero. Zero gradient conditions are used at the outlet.

The dimensionless externally imposed voltages at the inlets are specified as $\bar{\phi} = 1$. The outlet is grounded or $\bar{\phi} = 0$. All walls are assumed to be electrically non-conductive. The dimensionless concentration at one of the inlets is specified as $\bar{c} = 1$. The dimensionless concentration at the remaining inlet is set to zero. The zero axial gradient is used at the outlet.

2.2.3 Numerical Method

A multiblock approach is used to discretize the spatial domain into three blocks where high quality grids can be generated easily. Body-fitted coordinates are used within each block to model the complex shapes.

Body-fitted coordinates: The continuity (Eq. 2.1), momentum (Eq. 2.2), electric charge (Eq. 2.5), and concentration (Eq. 2.7) are special cases of the general transport equation; which when written in general body-fitted coordinates has the following form.

$$\frac{1}{J} \frac{\partial(\rho U \Phi)}{\partial \xi} + \frac{1}{J} \frac{\partial(\rho V \Phi)}{\partial \eta} = \frac{1}{J} \frac{\partial}{\partial \xi} \left[\frac{\Gamma}{J} \left(c_1 \frac{\partial \Phi}{\partial \xi} - c_2 \frac{\partial \Phi}{\partial \eta} \right) \right] + \frac{1}{J} \frac{\partial}{\partial \eta} \left[\frac{\Gamma}{J} \left(c_3 \frac{\partial \Phi}{\partial \eta} - c_2 \frac{\partial \Phi}{\partial \xi} \right) \right] + S \quad (2.10)$$

where

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$$U = u_x \frac{\partial y}{\partial \eta} - u_y \frac{\partial x}{\partial \eta} \quad (2.11a)$$

$$V = u_y \frac{\partial x}{\partial \xi} - u_x \frac{\partial y}{\partial \xi} \quad (2.11b)$$

$$c_1 = \left(\frac{\partial x}{\partial \eta} \right)^2 + \left(\frac{\partial y}{\partial \eta} \right)^2 \quad (2.11c)$$

$$c_1 = \frac{\partial x}{\partial \xi} \frac{\partial x}{\partial \eta} + \frac{\partial y}{\partial \xi} \frac{\partial y}{\partial \eta} \quad (2.11d)$$

$$c_3 = \left(\frac{\partial x}{\partial \xi} \right)^2 + \left(\frac{\partial y}{\partial \xi} \right)^2 \quad (2.11e)$$

$$J = \frac{\partial x}{\partial \xi} \frac{\partial y}{\partial \eta} - \frac{\partial y}{\partial \xi} \frac{\partial x}{\partial \eta} \quad (2.11f)$$

where Φ , ρ , Γ and S are the dependent variable, density, diffusion coefficient and source term respectively. The finite-volume method of Karki and Patankar (1989) is used to solve the transport equation given in Eq. (2.10). The covariant velocities are chosen as the dependent variables. The power-law of Patankar (1980) is used to model the combined convection-diffusion effect. The fully implicit scheme is used to discretize the transient term. The resulting algebraic equations are solved using the TriDiagonal Matrix Algorithm.

2.2.4 Multi-block Method

Multiblock methods in which the flow domain of interest is divided into several simple subdomains to facilitate the grid generation have been devised and widely used for Euler's equation and aerodynamic flow field calculations. For the internal flow computations, Yung *et al.* (2000) used the overlapping grid method with a staggered

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grid arrangement in calculating the diffuser flows. Fuchs *et al.* (2004) used the overlapping zones in calculating the two-dimensional multibranched flows. A SIMPLER-type algorithm calculation procedure together with a staggered grid arrangement in a boundary-fitted coordinate system was employed here.

One of the major advantages of using multiblock lies in the simplification of the grid generation procedure for a rather complex geometry, since a complex domain can be divided into a few simple geometry subdomains. As the development of concurrent computing algorithms proceeds, the multiblock method can become a very efficient and robust approach, since solutions can be advanced simultaneously in all the subdomains. The geometries encountered in an electrokinetic flow problem are in many cases very irregular and complex, therefore, use of the multiblock should be able to significantly reduce the effort needed for the grid generation. To our knowledge, multiblock has not yet been employed in the numerical simulations of electrokinetic flow problems. The present approach also can be conveniently extended to trifurcation or multibranching flows without difficulty.

High quality single block structured grid is difficult to generate for the Y-shaped micromixer considered (Fig. 2.1). As a result, the micromixer is divided into three blocks where high quality computational grids can be generated within each block. A multiblock procedure is used to ensure mass, momentum and species conservations over the whole micromixer. The transfer of information between two spatial blocks is described next. The following discussion is divided into three “classes” of variables.

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These are (1) u_ξ , (2) u_η and (3) scalar variables. Different treatments are needed for the two velocity components because the two velocities are staggered half a control volume from the scalar variables.

Figure 2.2 shows the three situations at the interfaces between two spatial blocks. Consider a multi-block grid composed of the two blocks with a ξ direction overlap region as shown in Figure 2.2. Block 1 is shown using solid lines while the second block is depicted using dashed lines. The solid and dashed lines are displaced slightly for clarity and ease of visualization. These lines coincide with each other in the actual computations. In this article, the two blocks overlap over the width of two control volumes as shown in Fig. 2.2. The interface where Block 1 ends is called II, while the interface where Block 2 ends is called I. The boundary values for Block 1 at II are obtained from the internal values of Block 2. Similarly, the boundary values of Block 2 are calculated from the internal values of Block 1.

2.2.4.1 u_ξ

As u_ξ is displaced half a control volume to the west, it lies on the interfaces I and II. As a result, no interpolations are needed to transfer the velocities. At interface II, the boundary velocities for Block 1 are set to the most current internal velocities in Block 2 as shown in Fig. 2.2a. The boundary velocities for Block 2 at I are set to the most current internal values of Block 1.

2.2.4.2 u_η

As u_η are staggered half a control volume to the south (Fig. 2.2b), these velocities do not lie on an interface. The interface values are obtained from the neighboring values. At interface I, the boundary value for Block 2 are set to the interface value of Block 1 namely, $u_{\eta,b,2} = u_{\eta,i,1}$. This interface value is in term obtained by interpolating between the two neighboring values namely, $u_{\eta,i,1} = f(u_{\eta,-,1}, u_{\eta,+,1})$. Similar approach is used at interface II.

2.2.4.3 Scalar Variables

All scalar variables are stored at the nodal locations as shown in Fig. 2.2c. As a result, all boundary values are interpolated from neighboring nodal values as shown in Fig. 2.2c. For example, at interface I, the boundary values for Block 2 are interpolated from the nodal values in Block 1 namely, $c_{b,2} = f(c_{-,1}, c_{+,1})$.

During the first iteration, the values of the velocities at the exits of the “upstream” blocks are set such that mass flow rate within the block is conserved. This is done because the velocities in a “downstream” block are yet to be determined.

Figure 2.2 Information transfer between two blocks, (a) u_ξ , (b) u_η and (c) scalar.

2.2.5 Solution Procedure

The solution procedure can be summarized as follows:

For $bn = 1, nb$

1. Update velocity such as u_ξ, u_η for internal block boundaries in order to conserve the mass globally.
2. Start with a guessed velocity field.
3. Solve the momentum equations to obtain $\hat{u}_\xi, \hat{u}_\eta$.
4. Solve the pressure equation and obtain the pressure field.
5. Treating this pressure field as p^* , solve the momentum equations to obtain u_ξ^*, u_η^* .
6. Calculate the mass source b and b_{NO} , and hence solve the pressure correction equation p' .
7. Correct the velocity field, but do not correct the pressure.
8. Update the other variables for the internal block boundaries and solve the discretization equations for other Φ 's if necessary.
9. Return to step 1 and repeat until convergence.

In this scheme, bn is the block that is to be executed and nb is the number of the blocks and the multi-block loop is the outer loop. All the equations are solved in one block, followed by an update of the information stored in the internal block boundaries from the neighboring blocks before proceeding to the next block in the domain.

2.3 Results and Discussions

2.3.1 Validation of the Numerical Scheme

2.3.1.1 Case 1: Shear-Driven Cavity Flow

The laminar incompressible flow in a square cavity with the top wall moving with a uniform velocity and other walls with no slip boundary condition has served as the benchmark solution for testing and evaluating numerical technique as reported by Ghia *et al.* (1982). In order to facilitate the exchange of information between the two blocks, two layers of extended control volumes are constructed at the common interface for each of the blocks.

The multiblock fluid flow of the conservative treatments of mass flux and momentum flux with varying accuracies are tested and compared. For the shear-driven cavity flow with $Re = 1000$, a two-block continuous body fitted grid configuration with different grid resolution is used. Four grid systems of $(40 \times 20$ and $40 \times 20)$, $(80 \times 40$ and $80 \times 40)$, $(120 \times 60$ and $120 \times 60)$, $(200 \times 100$ and $200 \times 100)$ for block I and block II are used respectively. Fig. 2.3 (a) show the body fitted grid arrangement. Fig. 2.3 (b) shows the streamline contours for the cavity flow with the body fitted grid 200×100 and 200×100 for block I and block II respectively. The various primary, secondary and corner vortices (Fig. 2.3(b)) are compared with Fig. 2.3(c) by Ghia *et al.* (1982). Good agreement can be seen. Figs. 2.3 (d) and 2.3 (e) show the u-component distributions

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(a)

(b)

(c)

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(d)

(e)

Figure 2.3(a) Two-block continuous body fitted grid

with 120×60 and 120×60 for block 1 and block 2;

(b) Streamline contours for $Re=1000$ with body fitted grid with

200×100 and 200×100 for block 1 and block 2;

(c) Streamline contours for $Re=1000$ (Ghia *et al.*, 1982);

(d) u velocity along the vertical center line;

(e) v velocity along the horizontal center line.

along the vertical center line and v-component distributions along the horizontal center line for four grid systems. They are compared with the corresponding benchmark solution reported by Ghia *et al.* (1982). It can be seen that the solutions improved as the grids are refined.

2.3.1.2 Case 2: T-shaped Micromixer

Figure 2.4 Computational meshes $\alpha = 180^\circ$

Species transport in a T-shaped micromixer examined by Erickson *et al.* (2002), is computed using the multiblock approach described in this work. The T-shaped micromixer is divided into three spatial blocks as shown in Fig. 2.4. The width w and length L_{arm} are set to $50\mu m$ and $50\mu m$. The length of the mixing channel, L_{mix} , is set to a value which ensures the two streams are fully mixed ($\bar{c} = 0.5$) at the outlet. For the cases investigated in this simulation, the L_{mix} is about 50 times the channel width. The zeta potential ζ , electroosmotic mobility and diffusion coefficient are -42 mV , $4 \times 10^{-8}\text{ m/Vs}$ and $3 \times 10^{-10}\text{ m}^2/s$ respectively. The external applied electric field (as defined in Eq. 2.12) is set to 500 V/cm .

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$$E_0 = \frac{\phi_{\max} - \phi_{\min}}{L_{\text{arm}} + L_{\text{mix}}}$$

(2.12)

For quantitative analysis, a mixing efficiency η is defined as

$$\eta = \left(1 - \frac{\int_0^w |\bar{c} - \bar{c}_\infty| dy}{\int_0^w |\bar{c}_0 - \bar{c}_\infty| dy} \right) \times 100\%$$

(2.13)

where $\bar{c}_0$ is the species concentration in the completely unmixed (can be either 0 or 1) and $\bar{c}_\infty$ is the species concentration in the completely mixed states (= 0.5). Figure 2.5 shows the mixing efficiencies along the L_{mix} for three cases. The present computations compare well with the results of Erickson *et al.* (2002).

Figure 2.5 Mixing efficiency for a T-shaped micromixer.

2.3.1.3 Case 3: Experimental Validation

In this section, we chose the set of experimental results reported by Yan (2007) to validate our mathematical model. The T-shaped micromixer fabricated by PDMS is shown in Figure 2.6. The micromixer has $L_{arm} = 0.5\text{ cm}$, $L_{mix} = 1\text{ cm}$. The cross sections of the arm channel and mixing channel are $150\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ and $300\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ respectively. The electroosmotic mobility and diffusion coefficient are $3.6 \times 10^{-8}\text{ m/Vs}$ and $3 \times 10^{-10}\text{ m}^2/\text{s}$ respectively. Pure water is at one of the inlets. Fluorescent dye also called Rhodamine B was added at the remaining inlet for the purpose of images collection. Fluorescence imaging and micro-PIV (micro particle image velocimetry) measurement were used in the experiment.

Figure 2.6 T-shaped micromixer used in the experiment (Yan, 2007)

Figures 2.7(a), (b) (c) and (d) show the comparison of the concentration profiles between the numerical simulation results and the experimental results at the four

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downstream distances 2 mm , 4 mm , 7 mm , 9 mm for the inlet electric potential is equal to 150 V . Reasonably good agreement is obtained.

Figure 2.7 Comparison between numerical simulation and experimental concentration profiles for different downstream distance (a) 2 mm (b) 4 mm (c) 7 mm (d) 9 mm

Figure 2.8 shows the mixing efficiency along the downstream distance between the

experimental results and the multiblock body-fitted numerical simulation for different applied electric fields. The comparison shows that the proposed numerical method can predict the mixing efficiency relatively well.

Figure 2.8 Comparison of the mixing efficiency for a T-shaped micromixer for different electric fields.

2.3.2 Y-shaped Micromixers

The influences of the inlet bifurcation angle (Fig. 2.1), of a Y-shaped micromixer on the species mixing efficiency are studied. Figures 2.9a and 2.9b show the computational grids for two bifurcation angles namely, 60° and 120°. The mixers are divided into three spatial blocks. As seen from the figures, the mesh skewness increases with bifurcation angle.

Figure 2.9 Computational meshes: (a) $\alpha = 60^\circ$ and (b) $\alpha = 120^\circ$.

In this part of the work, w , L_{arm} and L_{mix} are set to x , y and z respectively. The viscosity, density, dielectric constant and diffusion coefficient of the solution are $1.12 \times 10^{-3} \text{ kg/m}\cdot\text{s}$, 999 kg/m^3 , 80 and $10^{-10} \text{ m}^2/\text{s}$ respectively. The simulation assumes a homogeneous zeta potential, ζ of 25 mV . The external applied electric field is $E_0 = 100 \text{ V/cm}$. The channel width is $w = 50 \mu\text{m}$.

As seen from Fig. 2.9, the mesh skewness increases with bifurcation angle. As to grid independent, we choose the most severe case: the bifurcation angle α is 120° . A three-block continuous body fitted grid configuration with different grid resolution is used. Three grid systems of coarse grid (10×6 , 10×6 and 200×12), intermediate grid (20×12 , 20×12 and 400×24), fine grid (48×24 , 48×24 and 800×48) for block I, block II and block III are used respectively. Figure 2.10 (a) and (b) show the grid convergent study for mixing efficiency and concentration distribution. From

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all of the above results, we can conclude that this numerical method is suitable for the complex Y-shaped micromixer. In the following simulations, intermediate grid 20×12 , 20×12 and 400×24 for three blocks are used.

Figure 2.10 Grid convergent study (a) Mixing efficiency for a Y-shaped micromixer, $\alpha = 120^\circ$.

(b) Concentration distribution for a Y-shaped micromixer, $\alpha = 120^\circ$.

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Figure 2.11 shows the dimensionless electric potential distributions for three inlet bifurcating angles namely, $\alpha = 60^\circ$, 120° and 180° . The intersection is where the inlet channel and mixing channel meet. The results show that the dimensionless potential at the intersection for $\alpha = 60^\circ$ and 120° are 0.975. But the dimensionless potential for $\alpha = 180^\circ$ at the intersection is larger than 0.975.

Figure 2.11 Distributions of the dimensionless external electric potential.

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Figure 2.12 shows the local electrical potential gradient along the inlet channel, L_{arm} and the mixing channel, L_{mix} . The result shows that the electric fields change sharply around the intersection. The electric potential gradient increases along the inlet channel, L_{arm} for three different bifurcation angles. At the intersection, the electric potential gradient reaches the maximum. Then, the electric potential gradient decreases from the intersection to the mixing channel. Along the mixing channel L_{mix} , it is almost the same for the three bifurcation angles. Away from the intersection, the electric field is lower in the inlet channel than the mixing channel. It agrees well with the experiment that Paegel *et al.* (2002) found the constricted regions of channel turns have high electric fields. In general, constricting channels may cause increased Joule heating and temperature rise in the turn.

Figure 2.12 Electric potential gradients along the channel wall.

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Figure 2.13 shows the dimensionless concentration distributions of the two species for three bifurcation angles. The Peclet number and Reynolds number are 98.34 and 1.09×10^{-2} for different α . With the large Peclet number ($Pe > 100$), the diffusion effect is negligible compared to the convection. While with the small Peclet number ($Pe < 1$), the convection effects will be smaller than the diffusion effects and diffusion effect will be dominant. When the bifurcation angle increases from 60° to 120° , the diffusion distances are almost the same, a little larger than for $\alpha = 180^\circ$. The concentration is almost 0.5 after the downstream distance $900 \mu m$ for $\alpha = 60^\circ$ and

Figure 2.13 Concentration contours for three bifurcation angles.

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120°, approximately 800 μm for α=180°. So from the Fig. 2.14, we can see that the mixing efficiency is a little larger for α=180° than other inlet bifurcation angle.

Figure 2.14 Effects of bifurcation angle on mixing efficiency.

Fig. 2.15 compares the mixing efficiency in a 50 μm channel width with different electric field strength of 100 V/cm and 200 V/cm for bifurcation angles of 60° and 120°. The diffusion length across the width of the micromixer can be described by the Einstein equation (Einstein,1956),

$$L_{diff} = \sqrt{2Dt} \tag{2.14}$$

where D and t are the diffusion coefficient and the resident time, respectively. Note that the resident time for diffusive exchange between the two streams is controlled by the fluid velocity in the mixing channel. A lower electric field decreases the flow

Figure 2.15 Effect of different electric fields on the mixing efficiency of bifurcation angles 60° and 120° Y-shaped micromixer with $w = 50 \mu\text{m}$, $\zeta = 25 \text{ mV}$, $D = 1.0 \times 10^{-10} \text{ m}^2/\text{s}$.

velocity; the resident time of the sample streams within the mixing channel is increased. Hence when a lower electric field is applied, the mixing efficiency increased.

Fig. 2.16 compares the mixing efficiency in a $50 \mu\text{m}$ channel width with that $75 \mu\text{m}$ channel for both bifurcation angles of 60° and 120° cases. As the mixing is diffusive in nature for the small Peclet number, the diffusion flux f which is described in terms of the local concentration gradients as

$$f = D \frac{\nabla c}{w} \tag{2.15}$$

where w is the diffusion length scale. As expected that the smaller diffusion length,

Figure 2.16 Effect of different channel widths on the mixing efficiency of bifurcation angles

60° and 120° Y-shaped micromixer with

$$E_0 = 100 \text{ V/cm}, \zeta = 25 \text{ mV}, D = 1.0 \times 10^{-10} \text{ m}^2/\text{s}.$$

in the 50 μm channel leads to the greater concentration gradient and hence an increased diffusive flux and mixing efficiency over that exhibited by the 75 μm channel.

2.4 Summary

For low Reynolds number electroosmotic driven flows in microfluidic devices, species mixing is inherently diffusion dominated, leading to poor mixing efficiency or requiring long transport distances. The experimental data of T-shaped micromixer for different electric field were used to validate multiblock 2D body fitted finite volume simulation. In this work, the effects of the inlet bifurcation angle on the mixing

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efficiency of Y-shaped micromixer was investigated through the 2D body fitted, multi-block numerical simulations. The simulation results demonstrate that altering the angle between the inlet channels does not affect the mixing efficiency. The constricted regions of channel turns have high electric fields.

CHAPTER 3

Electrokinetic instability in micromixing

3.1 Introduction

Many of the lab-on-a-chip microfluidic devices apply electrokinetic liquid phase for mixing, transportation and separation of samples. Electrolytes of interest may be inhomogeneous; hence concentration mismatches often occur between the samples and the buffers solutions. For example, in the sample stacking process (Yabg and Chien, 2001) inhomogeneous samples streams with different concentrations are used. As two inhomogeneous electrolytes of different concentrations are subjected to an applied electric field, instabilities occur if the strength of the applied electric field exceeds the threshold value (Lin *et al.*, 2004; Chen *et al.*, 2005; Oddy *et al.*, 2005). Electrokinetic instabilities (EKI) are caused by the ionic conductivity gradient and applied electric fields. The interaction of electric field and conductivity gradient results in an electric body force in the bulk liquid that can generate temporal, convective and absolute flow instabilities (Posner *et al.*, 2006; Chen *et al.*, 2005; Oddy *et al.*, 2005).

Electrokinetic instability is treated as a specialized form of electrohydrodynamic instability that is coupled with electroosmotic flow. Relevant to the mechanism of instability, the pioneering work started with Taylor and Melcher (1969) for establishing the leaky dielectric model. Hoburg and Melcher (1977) observed that applying electric

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fields transverse to a conductivity gradient in a flow cell created an interface of ionically doped and undoped corn oil, electrohydrodynamic instability occurs as a results of charge accumulation at material interfaces and the interaction of the applied field and conductivity gradients. Baygents and Baldessari (1998) performed a linear stability analysis on a quiescent thin layer of liquid in which the electrical conductivity varies linearly over the depth of the layer. The conditions for marginal stability were determined; the analysis shows that the relevant dimensionless groups are the electric Rayleigh number, relative conductivity increment, the ratio of viscous to charge relaxation times and the transverse wave number of the disturbance.

Santiago's group has contributed linear and experimental analysis to understand the electrokinetic instability. Lin and Santiago (2004) analyzed the two dimensional linear stability analysis of the two-ion SBE (symmetric binary electrolyte) model and conducted nonlinear flow simulations. They show that the model provides good qualitative and fair quantitative agreement with regard to the threshold electric field and critical wave number for a conductivity ratio 10. Chen and Santiago (2005) demonstrated that electroosmotic flow in electrokinetic systems leads to convective and absolute instabilities. When the internally generated electroviscous velocity disturbances are high enough to overcome electroosmotic convection, there is absolute instability. Both the electroviscous and electroosmotic velocities result from balancing electric body forces and viscous stresses. Story *et al.* (2005) developed a thin channel model for fluid flow and compared the model with a three dimensional models. They find good agreement between these models. Oddy and Santiago (2005) considered a multiple species model that can be used

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to analyze either SBE or non-SBE systems. Posner and Santiago (2006) used quantitative epifluorescence imaging for experimental study of convective electrokinetic instability in an isotropically etched, cross-shaped microchannel.

Shin *et al.* (2005) applied a time-periodic electric field to excite the instability in a cross channel. Through the frequency sweeping from 0.1 Hz to 50 Hz, they found that the instability is most enhanced when the period of the applied electric field is close to half of the period of instability in the form of a sinusoidal wave generated under a static electric field. Park *et al.* (2005) found that the mixing efficiency is increased by about 15% for the channel with herringbone-shape cavities as compared with the straight channel.

In this chapter, we report the linear stability analysis and numerical simulation of the electrokinetic flow instability in microchannels. First, we present a temporal linear stability analysis and obtained a critical electric field for the electrokinetic instability associated with the concentration gradient. A variety of correlation coefficient, zeta potential, diffusivity, and concentration ratio will be examined with the goal of determining the critical electric field for the electrokinetic instability. We also adopted the numerical simulation for revealing the evolution processes of the electrokinetic instability for different electric field. The linear stability analysis and numerical simulation help to determine the nature of instability and unfold the physics of the instability. The concentration gradient and charge accumulation at the interface region are the key instability mechanism.

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3.2 Mathematical Formulation

3.2.1 Governing Equations

3.2.1.1 Conservation of Mass

In fluid dynamics, a continuity equation is an equation of conservation of mass. Its differential form is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0 \quad (3.1)$$

where ρ is fluid density.

Under the incompressible assumption, density is a constant and it follows that the equation will simplify to:

$$\nabla \cdot \vec{V} = 0 \quad (3.2)$$

3.2.1.2 Conservation of Momentum

In the liquid, electrostatic phenomena and hydrodynamics are coupled by the Maxwell's stress tensor. In a dielectric medium without magnetic contribution, the Maxwell's stress tensor is expressed as (Savile, 1984)

$$\mathbf{T}^M = \epsilon_r \epsilon_0 \vec{E} \vec{E} - \frac{1}{2} \epsilon_r \epsilon_0 \left[1 - \frac{\rho}{\epsilon_r} \left(\frac{\partial \epsilon_r}{\partial \rho} \right)_T \right] (\vec{E} \cdot \vec{E}) \mathbf{I} \quad (3.3)$$

where ϵ_r and $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}/(\text{N} \cdot \text{m}^2)$ are the relative permittivity and the vacuum permittivity respectively. Here $\vec{E} = -\nabla \phi$ is the electric field strength, where ϕ is the

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electrostatic potential. $\left(\frac{\partial \varepsilon_r}{\partial \rho}\right)_T$ is the change in relative permittivity with density at constant

temperature.

The bulk balance law for momentum

$$\frac{\partial(\rho \vec{V})}{\partial t} + \nabla \cdot (\rho \vec{V} \vec{V}) = \nabla \cdot (\mathbf{T} + \mathbf{T}^M) + \rho \mathbf{f} \quad (3.4)$$

where $\mathbf{f}$ is the body force, $\mathbf{T}$ is the stress tensor (incompressible liquid) (White, 1991)

$$T_{ij} = -P\delta_{ij} + \mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (3.5)$$

where μ is the viscosity.

For an incompressible liquid, expanding the Maxwell stress tensor and the stress tensor for incompressible Newtonian liquids yields

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho(\vec{V} \cdot \nabla) \vec{V} = -\nabla \cdot \left[P - \frac{1}{2} \varepsilon_0 \rho \left(\frac{\partial \varepsilon_r}{\partial \rho} \right)_T \vec{E} \cdot \vec{E} \right] - \frac{1}{2} \varepsilon_0 \vec{E} \cdot \vec{E} \nabla \varepsilon_r + \rho_e \vec{E} + \mu \nabla^2 \vec{V} \quad (3.6)$$

In this equation, the presence of the inhomogeneous dielectric permeability and net volume charges work as the body force for liquids. To simplify, we consider constant permeability in the whole fluid dielectric. Eq. (3.6) reduces

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho(\vec{V} \cdot \nabla) \vec{V} = -\nabla P + \rho_e \vec{E} + \mu \nabla^2 \vec{V} \quad (3.7)$$

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The electric field is assumed to be quasi static and is related to electric potential ϕ by

$$\vec{E} = -\nabla\phi \quad (3.8)$$

The charge distribution with the externally applied electric field potentials generates an electric field within the liquid; the spatial variation of the electric field can be specified by the Poisson's equation.

$$\nabla \cdot (\epsilon \vec{E}) = \rho_e \quad (3.9)$$

Assuming the permittivity of the liquid is uniform, the electrostatic potential ϕ is related with the charge density as

$$\rho_e = -\epsilon \nabla^2 \phi \quad (3.10)$$

So the Eq. (3.6) becomes

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \cdot \nabla) \vec{V} = -\nabla P + \epsilon \nabla^2 \phi \nabla \phi + \mu \nabla^2 \vec{V} \quad (3.11)$$

3.2.1.3 Conservation of Species

The transport equations for positive and negative species give

$$\frac{\partial c}{\partial t} + \vec{V} \cdot \nabla c = D_+ \nabla^2 c + \frac{Fz_+ D_+}{RT} \nabla \cdot (c \nabla \phi) \quad (3.12(a))$$

$$\frac{\partial c}{\partial t} + \vec{V} \cdot \nabla c = D_- \nabla^2 c + \frac{Fz_- D_-}{RT} \nabla \cdot (c \nabla \phi) \quad (3.12(b))$$

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where D_+ and D_- are the diffusion coefficients of the positive and negative species. R and T are the gas constant and temperature respectively. F denotes Faraday's constant and z_+ and z_- are the valence number of the positive and negative species. ϕ is the electrostatic potential. $\vec{V}$ is the velocity.

Subtracting the equation for the positive ions Eq.(3.12(a)) from that for the negative ions Eq.(3.12(b)) gives

$$\frac{F}{RT}(z_-D_- - z_+D_+)\nabla \cdot (c\nabla \phi) + (D_- - D_+)\nabla^2 c = 0 \quad (3.13)$$

This relation can be used to eliminate the electric potential from either the positive or negative ion convective diffusive equation. So the convective diffusion equation yields

$$\frac{\partial c}{\partial t} + \vec{V} \cdot \nabla c = D_{eq} \nabla^2 c \quad (3.14)$$

Eq. (3.14) describes the concentration distribution in the dilute binary electrolyte incorporating the effect of current flow that is the same as the convective diffusion equations for a neutral species. The effective diffusion coefficient D_{eq} is defined as

$$D_{eq} = \frac{z_+D_+D_- - z_-D_-D_+}{z_+D_+ - z_-D_-} \quad (3.15)$$

3.2.1.4 Conservation of Charge

For dilute solutions the flux contributions from the electromigration, diffusion and convection can be linearly superposed, we have for the molar flux of the i th species

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$$\vec{j}_i = -m_i z_i F c_i \nabla \phi - D_i \nabla c_i + c_i \vec{V} \quad (3.16)$$

where m_i is molar conductivity and it measures how “mobile” the charged particles are in an electric field which is related to the diffusivity D_i by the relation $m_i = \frac{D_i}{RT}$. c_i is the concentration of the i species.

The first term on the right-hand side (RHS) of the Eq. (3.16) represents electromigration. Under the action of an applied electric field, unequal electrical forces act on different species due to the differences in species charge. The second term on the RHS represents diffusion of charge due to the concentration gradient. The third term represents convection of free charge.

Because of the motion of the charged species, there will be a current. The current density is given by $\vec{i} = F \sum z_i \vec{j}_i$. Apply the dilute solution relation for the molar flux

$$\vec{i} = -F^2 \sum \frac{z_i^2 D_i c_i}{RT} \nabla \phi - F \sum z_i D_i \nabla c_i + F \vec{V} \sum z_i c_i \quad (3.17)$$

The electrical conductivity of the solution is related to concentration of cations and anions, mobility (m) and valence number (z) as

$$\sigma = F^2 \sum z_i^2 m_i c_i \quad (3.18)$$

So the current can also be expressed as

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$$\vec{i} = -\sigma \nabla \phi - F \sum z_i D_i \nabla c_i + F \vec{V} \sum z_i c_i \quad (3.19)$$

The current is made up of contributions from the electric field, the concentration gradient and convection of charge. On using the conservation of charge $\nabla \cdot \vec{i} = 0$, we get

$$\nabla \cdot \left(-\frac{F^2 \sum z_i^2 D_i c_i}{RT} \nabla \phi - F \sum z_i D_i \nabla c_i \right) = 0 \quad (3.20)$$

For simplicity, we consider the symmetric electrolytes, with valence of the cations equal to the valence of the anions, $z_+ = z_- = 1$. Eq. (3.20) gives

$$\nabla \cdot (c \nabla \phi) = M \nabla^2 c \quad (3.21)$$

where $M = \frac{RT}{F} \frac{D_- - D_+}{D_- + D_+}$ is a constant.

The charge density is proportional to the sum of the ionic concentration of all the ions present

$$\rho_e = F \sum z_i c_i \quad (3.22)$$

To summarize the governing equations on continuity, momentum, species and charge conservation transport for incompressible, isothermal, electrokinetic microflows of dilute binary electrolyte are depicted as follows,

$$\nabla \cdot \vec{V} = 0 \quad (3.23(a))$$

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \cdot \nabla) \vec{V} = -\nabla P + \mu \nabla^2 \vec{V} + \epsilon \nabla^2 \phi \nabla \phi \quad (3.23(a))$$

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$$\frac{\partial c}{\partial t} + \vec{V} \cdot \nabla c = D_{eq} \nabla^2 c \quad (3.23(c))$$

$$\nabla \cdot (c \nabla \phi) = M \nabla^2 c \quad (3.23(d))$$

3.2.2 Boundary and Initial Conditions

We shall prescribe the following boundary conditions on the wall:

$$\vec{V} \cdot \mathbf{n} = 0 \quad (3.24(a))$$

$$\vec{V} \cdot \mathbf{t} = -\frac{\varepsilon E \zeta}{\mu} \quad (3.24(b))$$

$$\nabla c \cdot \mathbf{n} = 0 \quad (3.24(c))$$

$$\nabla \phi \cdot \mathbf{n} = 0 \quad (3.24(d))$$

where $\mathbf{t}$ and $\mathbf{n}$ are tangential and normal vectors of the wall. The wall is non-conductive and impenetrable and there is no ion diffusion across the boundaries.

Zeta potential is related to ionic concentration. The following correlation is assumed

$$\frac{\zeta}{\zeta_r} = \left(\frac{c}{c_r} \right)^n \quad (3.25)$$

where n is a correlation coefficient, c_r and ζ_r are reference concentration and zeta potential. The concentration interface is assumed to be uniform and the initial concentration is approximately

$$c(y) = \begin{cases} c_h & 0 \leq y \leq 1 \\ c_l & -1 \leq y \leq 0 \end{cases} \quad (3.26)$$

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Eqs. (3.23(a)) to (3.23(d)), together with appropriate boundary conditions Eqs. (3.24(a)) to (3.24(d)) and initial condition (3.26), completely define our system of interest.

3.3 Linear Stability Analysis

The system considered is shown in Fig. 3.1 and consists of two electrolytes with different concentrations c_h and c_l flow side-by-side within a microchannel. It is assumed that the channel depth ($2h$) in the z -direction is shallow compared to the channel width ($2w$) in the y -direction. An external electric field (E_0) is applied along the channel length in the x -direction.

Figure 3.1 Schematic of the analysis

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3.3.1 Governing Equations

3.3.1.1 Linearization of the Governing Equations

In linear stability analysis we assume that the perturbations to the base state are infinitesimally small. To carry out a linear stability analysis, the following perturbation variables are introduced:

$$u = u_0 + \tilde{u} \quad (3.27(a))$$

$$v = v_0 + \tilde{v} \quad (3.27(b))$$

$$w = w_0 + \tilde{w} \quad (3.27(c))$$

$$\phi = \phi_0 + \tilde{\phi} \quad (3.27(d))$$

$$P = P_0 + \tilde{P} \quad (3.27(e))$$

$$c = c_0 + \tilde{c} \quad (3.27(f))$$

where the $\sim$ denotes the perturbation quantities and subscripts '0' denotes the base state.

Substitute Eqs. (3.27) into the governing Eqs. (3.23) and invoke boundary conditions, the set of equations are then linearized neglecting higher order terms. We can obtain the linearized equations governing the disturbances.

$$\frac{\partial \tilde{u}}{\partial x} + \frac{\partial \tilde{v}}{\partial y} + \frac{\partial \tilde{w}}{\partial z} = 0 \quad (3.28(a))$$

$$\rho \frac{\partial \tilde{u}}{\partial t} + \rho u_0 \frac{\partial \tilde{u}}{\partial x} + \rho \tilde{v} \frac{\partial u_0}{\partial y} = -\frac{\partial \tilde{P}}{\partial x} + \mu \left(\frac{\partial^2 \tilde{u}}{\partial x^2} + \frac{\partial^2 \tilde{u}}{\partial y^2} + \frac{\partial^2 \tilde{u}}{\partial z^2} \right) + \varepsilon \left(\frac{\partial^2 \tilde{\phi}}{\partial x^2} + \frac{\partial^2 \tilde{\phi}}{\partial y^2} + \frac{\partial^2 \tilde{\phi}}{\partial z^2} \right) \frac{\partial \phi_0}{\partial x} \quad (3.28(b))$$

$$\rho \frac{\partial \tilde{v}}{\partial t} + \rho u_0 \frac{\partial \tilde{v}}{\partial x} = -\frac{\partial \tilde{P}}{\partial y} + \mu \left(\frac{\partial^2 \tilde{v}}{\partial x^2} + \frac{\partial^2 \tilde{v}}{\partial y^2} + \frac{\partial^2 \tilde{v}}{\partial z^2} \right) \quad (3.28(c))$$

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$$\rho \frac{\partial \tilde{w}}{\partial t} + \rho u_0 \frac{\partial \tilde{w}}{\partial x} = -\frac{\partial \tilde{P}}{\partial z} + \mu \left(\frac{\partial^2 \tilde{w}}{\partial x^2} + \frac{\partial^2 \tilde{w}}{\partial y^2} + \frac{\partial^2 \tilde{w}}{\partial z^2} \right) \quad (3.28(d))$$

$$\frac{\partial \tilde{c}}{\partial t} + u_0 \frac{\partial \tilde{c}}{\partial x} + \tilde{v} \frac{\partial c_0}{\partial y} = D_{eq} \left(\frac{\partial^2 \tilde{c}}{\partial x^2} + \frac{\partial^2 \tilde{c}}{\partial y^2} + \frac{\partial^2 \tilde{c}}{\partial z^2} \right) \quad (3.28(e))$$

$$\frac{\partial \tilde{c}}{\partial x} \frac{\partial \phi_0}{\partial x} + \frac{\partial c_0}{\partial y} \frac{\partial \tilde{\phi}}{\partial y} + c_0 \left(\frac{\partial^2 \tilde{\phi}}{\partial x^2} + \frac{\partial^2 \tilde{\phi}}{\partial y^2} + \frac{\partial^2 \tilde{\phi}}{\partial z^2} \right) = M \left(\frac{\partial^2 \tilde{c}}{\partial x^2} + \frac{\partial^2 \tilde{c}}{\partial y^2} + \frac{\partial^2 \tilde{c}}{\partial z^2} \right) \quad (3.28(f))$$

3.3.1.2 Dimensionless Disturbance Equations

The linearized disturbance Eqs. (3.28) can be nondimensionalized by introducing the dimensionless parameters below.

$$\begin{aligned} x, y &\sim w & z &\sim h & c_0, \tilde{c} &\sim c_r \\ \tilde{V}_0 &\sim V_{EO} & t &\sim w/V_{EO} & \tilde{\phi} &\sim E_0 w \\ \tilde{u}, \tilde{v} &\sim V_{EV} & \tilde{w} &\sim \delta V_{EV} & \tilde{P} &\sim \mu V_{EV} w / h^2 \\ Pe &= \frac{w V_{EO}}{D_{eq}} & Re &= \frac{\rho V_{EO} w}{\mu} & \delta &= h / w \\ G_1 &= \frac{\varepsilon E_0^2 w}{\mu V_{EV}} & G_2 &= \frac{M}{w E_0} & EV_{EO} &= \frac{V_{EV}}{V_{EO}} = \frac{E_0 w}{\zeta_0} \end{aligned} \quad (3.29)$$

Here, the obvious velocity scale in the electroosmotic flow is known as the *Helmholtz-Smoluchowski* velocity:

$$V_{EO} = \frac{\varepsilon E_0 \zeta_0}{\mu} \quad (3.30)$$

Electrokinetic instabilities are internally driven processes. Hoburg and Melcher (1976)

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provided the electroviscous velocity scale. This velocity scale is derived from the balance viscous force with the electric body force in the momentum equation, following Hoburg and Melcher (1976):

$$V_{EV} = \frac{\epsilon E_0^2 w}{\mu} \quad (3.31)$$

Using the reference scales listed above, the dimensionless disturbance equations of mass, momentum conservation equations, species conservation, charge conservation become

$$\frac{\partial \tilde{u}}{\partial x} + \frac{\partial \tilde{v}}{\partial y} + \frac{\partial \tilde{w}}{\partial z} = 0 \quad (3.32(a))$$

$$\text{Re} \delta^2 \left(\frac{\partial \tilde{u}}{\partial t} + u_0 \frac{\partial \tilde{u}}{\partial x} + \tilde{v} \frac{\partial u_0}{\partial y} \right) = -\frac{\partial \tilde{P}}{\partial x} + \delta^2 \left(\frac{\partial^2 \tilde{u}}{\partial x^2} + \frac{\partial^2 \tilde{u}}{\partial y^2} \right) + \frac{\partial^2 \tilde{u}}{\partial z^2} - G_1 \delta^2 \left(\frac{\partial^2 \tilde{\phi}}{\partial x^2} + \frac{\partial^2 \tilde{\phi}}{\partial y^2} \right) - G_1 \frac{\partial^2 \tilde{\phi}}{\partial z^2} \quad (3.32 (b))$$

$$\text{Re} \delta^2 \left(\frac{\partial \tilde{v}}{\partial t} + u_0 \frac{\partial \tilde{v}}{\partial x} \right) = -\frac{\partial \tilde{P}}{\partial y} + \delta^2 \left(\frac{\partial^2 \tilde{v}}{\partial x^2} + \frac{\partial^2 \tilde{v}}{\partial y^2} \right) + \frac{\partial^2 \tilde{v}}{\partial z^2} \quad (3.32 (c))$$

$$\text{Re} \delta^4 \left(\frac{\partial \tilde{w}}{\partial t} + u_0 \frac{\partial \tilde{w}}{\partial x} \right) = -\frac{\partial \tilde{P}}{\partial z} + \delta^4 \left(\frac{\partial^2 \tilde{w}}{\partial x^2} + \frac{\partial^2 \tilde{w}}{\partial y^2} \right) + \delta^2 \frac{\partial^2 \tilde{w}}{\partial z^2} \quad (3.32(d))$$

$$Pe \delta^2 \left(\frac{\partial \tilde{c}}{\partial t} + u_0 \frac{\partial \tilde{c}}{\partial x} + EV_{EO} \tilde{v} \frac{\partial c_0}{\partial y} \right) = \delta^2 \left(\frac{\partial^2 \tilde{c}}{\partial x^2} + \frac{\partial^2 \tilde{c}}{\partial y^2} \right) + \frac{\partial^2 \tilde{c}}{\partial z^2} \quad (3.32(e))$$

$$\delta^2 \left(-\frac{\partial \tilde{c}}{\partial x} + \frac{\partial c_0}{\partial y} \frac{\partial \tilde{\phi}}{\partial y} + c_0 \left(\frac{\partial^2 \tilde{\phi}}{\partial x^2} + \frac{\partial^2 \tilde{\phi}}{\partial y^2} \right) \right) + c_0 \frac{\partial^2 \tilde{\phi}}{\partial z^2} = \delta^2 G_2 \left(\frac{\partial^2 \tilde{c}}{\partial x^2} + \frac{\partial^2 \tilde{c}}{\partial y^2} \right) + G_2 \frac{\partial^2 \tilde{c}}{\partial z^2} \quad (3.32(f))$$

3.3.1.3 Depth-Averaged Disturbance Equations

Lin's 2D linear model (2004) under-predicts the threshold electric field. But a 3D linear stability model is so complex that need much more computation time. In the experiment reported by Chen *et al.* (2005), the channel depth (h) in the z -direction is shallow compared to the channel width (w) in the y -direction. Thus, to simplify Eqs. (3.32) to include the leading order terms (Storey *et al.*, 2005; Oddy *et al.*, 2005), all variables are

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assume to follow an expansion of the form $f = f_0 + \delta f_1 + \delta^2 f_2 + \dots$ where $\delta = h/w$. The leading order terms are depth-averaged using the operation:

$$\bar{f}(x, y, t) = \frac{1}{2} \int_{-1}^1 \tilde{f}(x, y, z, t) dz \quad (3.33)$$

It is noted that the z -component velocity $\tilde{w}$ disappears after depth averaging ($\tilde{w}|_{z=\pm 1} = 0$).

Because the channel height to width ratio $\delta = h/w \ll 1$, we consider the leading order terms.

Leading order terms of Eq. (3.32(e))

$$\frac{\partial^2 \tilde{c}}{\partial z^2} = 0 \quad (3.34(a))$$

Together with the boundary condition

$$\left. \frac{\partial \tilde{c}}{\partial z} \right|_{z=\pm 1} = 0 \quad (3.34(b))$$

$$\text{Hence } \tilde{c} = \bar{c}(x, y, t) \quad (3.34(c))$$

The depth-averaged concentration disturbance is a function of x, y and t .

Leading order terms of Eq. (3.32(f))

$$c_0 \frac{\partial^2 \tilde{\phi}}{\partial z^2} - G_2 \frac{\partial^2 \tilde{c}}{\partial z^2} = 0 \quad (3.35(a))$$

$$\frac{\partial^2 \tilde{\phi}}{\partial z^2} = 0 \quad (3.35(b))$$

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Together with the boundary condition

$$\left. \frac{\partial \tilde{\phi}}{\partial z} \right|_{z=\pm 1} = 0 \quad (3.35(c))$$

Hence

$$\tilde{\phi} = \bar{\bar{\phi}}(x, y, t) \quad (3.35(d))$$

Leading order terms of Eq. (3.32(d))

$$-\frac{\partial \tilde{P}}{\partial z} = 0 \quad (3.36(a))$$

Hence

$$\tilde{P} = \bar{\bar{P}}(x, y, t) \quad (3.36(b))$$

Leading order terms of Eq. (3.32(c))

$$\frac{\partial^2 \tilde{v}}{\partial z^2} = \frac{\partial \tilde{P}}{\partial y} \quad (3.37(a))$$

Since the right hand side of Eq. (3.37(a)) is not a function of z , we can integrate to

obtain the velocity as a function of z and the depth averaged velocity $\bar{\bar{v}}$ as

$$\tilde{v} = \frac{\partial \tilde{P}}{\partial y} \frac{z^2 - 1}{2} + V_{EO} \quad (3.37(b))$$

$$\bar{\bar{v}} = \frac{1}{2} \int_{-1}^1 \tilde{v} dz = -\frac{1}{3} \frac{\partial \tilde{P}}{\partial y} + V_{EO} \quad (3.37(c))$$

Hence

$$\frac{\partial^2 \tilde{v}}{\partial z^2} = \frac{\partial \tilde{P}}{\partial y} = -3(\bar{\bar{v}} - V_{EO}) \quad (3.37(d))$$

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$$\text{where } V_{EO} = -\frac{u_0}{EV_{EO}} \frac{\partial \tilde{\phi}}{\partial y} \quad (3.37(e))$$

Leading order terms of Eq. (3.32(b))

$$\frac{\partial^2 \tilde{u}}{\partial z^2} = \frac{\partial \tilde{P}}{\partial x} + G_1 \text{Re} \frac{\partial^2 \tilde{\phi}}{\partial z^2} \quad (3.38(a))$$

Since the right hand side of Eq. (3.38(a)) is not a function of z , we can integrate to obtain the velocity as a function of z and the depth averaged velocity $\bar{\tilde{u}}$ as

$$\tilde{u} = \frac{z^2 - 1}{2} \left(\frac{\partial \tilde{P}}{\partial x} + G_1 \text{Re} \frac{\partial^2 \tilde{\phi}}{\partial z^2} \right) + U_{EO} \quad (3.38(b))$$

$$\bar{\tilde{u}} = \frac{1}{2} \int_{-1}^1 \tilde{u} dz = -\frac{1}{3} \left(\frac{\partial \tilde{P}}{\partial x} + G_1 \text{Re} \frac{\partial^2 \tilde{\phi}}{\partial z^2} \right) + U_{EO} \quad (3.38(c))$$

Hence

$$\frac{\partial^2 \tilde{u}}{\partial z^2} = \frac{\partial \tilde{P}}{\partial x} + G_1 \text{Re} \frac{\partial^2 \tilde{\phi}}{\partial z^2} = -3(\bar{\tilde{u}} - U_{EO}) \quad (3.38(d))$$

$$\text{where } U_{EO} = -\frac{u_0}{EV_{EO}} \frac{\partial \tilde{\phi}}{\partial x} \quad (3.38(e))$$

The dimensionless depth averaged disturbance equations are shown below:

$$\frac{\partial \bar{\tilde{u}}}{\partial x} + \frac{\partial \bar{\tilde{v}}}{\partial y} = 0 \quad (3.39(a))$$

$$\text{Re} \delta^2 \left(\frac{\partial \bar{\tilde{u}}}{\partial t} + \bar{u}_0 \frac{\partial \bar{\tilde{u}}}{\partial x} + \bar{v} \frac{\partial \bar{u}_0}{\partial y} \right) = -\frac{\partial \bar{\tilde{P}}}{\partial x} + \delta^2 \left(\frac{\partial^2 \bar{\tilde{u}}}{\partial x^2} + \frac{\partial^2 \bar{\tilde{u}}}{\partial y^2} \right) - 3(\bar{\tilde{u}} - U_{EO}) - G_1 \delta^2 \left(\frac{\partial^2 \bar{\tilde{\phi}}}{\partial x^2} + \frac{\partial^2 \bar{\tilde{\phi}}}{\partial y^2} \right) \quad (3.39(b))$$

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$$\text{Re} \delta^2 \left(\frac{\partial \bar{v}}{\partial t} + \bar{u}_0 \frac{\partial \bar{v}}{\partial x} \right) = -\frac{\partial \bar{P}}{\partial y} + \delta^2 \left(\frac{\partial^2 \bar{v}}{\partial x^2} + \frac{\partial^2 \bar{v}}{\partial y^2} \right) - 3(\bar{v} - V_{EO}) \quad (3.39(c))$$

$$Pe \left(\frac{\partial \bar{c}}{\partial t} + \bar{u}_0 \frac{\partial \bar{c}}{\partial x} + EV_{EO} \bar{v} \frac{\partial \bar{c}_0}{\partial y} \right) = \frac{\partial^2 \bar{c}}{\partial x^2} + \frac{\partial^2 \bar{c}}{\partial y^2} \quad (3.39(d))$$

$$-\frac{\partial \bar{c}}{\partial x} + \frac{\partial \bar{c}_0}{\partial y} \frac{\partial \bar{\phi}}{\partial y} + \bar{c}_0 \left(\frac{\partial^2 \bar{\phi}}{\partial x^2} + \frac{\partial^2 \bar{\phi}}{\partial y^2} \right) = G_2 \left(\frac{\partial^2 \bar{c}}{\partial x^2} + \frac{\partial^2 \bar{c}}{\partial y^2} \right) \quad (3.39(e))$$

3.3.1.4 Eigenvalue Solution

The linearized depth averaged disturbance Eqs. (3.39) can be arranged as a system of equations that are first order in x and t in a matrix form as showed in Eq. (3.40) .

$$\mathbf{N} \frac{\partial}{\partial t} [\mathbf{a}] = \frac{\partial}{\partial x} [\mathbf{a}] - \mathbf{M} [\mathbf{a}] \quad (3.40)$$

where $\mathbf{a}$ is a 8×1 matrix which contains the perturbation quantities

$$\mathbf{a} = \left(\bar{P}, \bar{u}, \bar{v}, \frac{\partial \bar{v}}{\partial x}, \bar{c}, \frac{\partial \bar{c}}{\partial x}, \bar{\phi}, \frac{\partial \bar{\phi}}{\partial x} \right)^T,$$

$\mathbf{N}$ and $\mathbf{M}$ are 8×8 matrix operators. $\frac{\partial}{\partial t}$ and $\frac{\partial}{\partial x}$ are differential operator.

$$\mathbf{N} = \begin{pmatrix} 0 & -\text{Re} \delta^2 & 0 & 0 & -\frac{G_1 G_2 Pe \delta^2}{\bar{c}_0} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \text{Re} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & Pe & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{\bar{c}_0} G_2 Pe & 0 & 0 & 0 \end{pmatrix}$$

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$$\mathbf{M} = \begin{pmatrix} 0 & -3 + \delta^2 D^2 & \left(\text{Re} \delta^2 \bar{u}_0 D - \text{Re} \delta^2 \frac{\partial \bar{u}_0}{\partial y} - \frac{G_1 G_2 \text{Pe} \delta^2 E V_{EO}}{\bar{c}_0} \frac{\partial \bar{c}_0}{\partial y} \right) & -\delta^2 D & 0 & \frac{G_1 \delta^2}{\bar{c}_0} (-G_2 \text{Pe} \bar{u}_0 - 1) & \frac{G_1 \delta^2}{\bar{c}_0} \frac{\partial \bar{c}_0}{\partial y} D & -\frac{1}{E} \\ 0 & 0 & -D & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ \frac{D}{\delta^2} & 0 & 3/\delta^2 - D^2 & \text{Re} \bar{u}_0 & 0 & 0 & \frac{3\bar{u}_0}{\delta^2 E V_{EO}} D & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & \text{Pe} E V_{EO} \frac{\partial \bar{c}_0}{\partial y} & 0 & -D^2 & \text{Pe} \bar{u}_0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & G_2 \text{Pe} E V_{EO} \frac{1}{\bar{c}_0} \frac{\partial \bar{c}_0}{\partial y} & 0 & 0 & \frac{1}{\bar{c}_0} (G_2 \text{Pe} \bar{u}_0 + 1) & \left(-\frac{1}{\bar{c}_0} \frac{\partial \bar{c}_0}{\partial y} D - D^2 \right) & 0 \end{pmatrix}$$

where D represents the differential operator in y , i.e. $\frac{\partial}{\partial y}$. $\mathbf{N}$ and $\mathbf{M}$ are linear matrix

operators depends on the base state and a set of control parameters such as the Re and Pe number. $\mathbf{N}$ and $\mathbf{M}$ are homogeneous in time t (space variable x). Homogeneity with respect to time and space coordinates allows us to make extensive use of Fourier-Laplace transforms to effectively reduce the stability problem (3.40) to an ordinary differential or algebraic equation (Godréche, 1998, P.120).

The perturbation quantities are further expressed in terms of normal modes. A spatially and temporally periodic perturbation can be assumed in the form:

$$\bar{\mathbf{a}}(x, y, t) = \hat{\mathbf{a}}(y) e^{i(kx - \omega t)} \quad (3.41)$$

Such solutions are possible since the linear operators are homogeneous in space and time.

When the normal modes are inserted into Eq. (3.40), the systems of Eq. (3.40) are transformed to an eigenvalue problem by replacing $\partial/\partial t$ by $-i\omega$ and $\partial/\partial x$ by ik .

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$$i\omega \mathbf{N}\hat{\mathbf{a}}(y) = \{\mathbf{M} - ik\mathbf{I}\} \hat{\mathbf{a}}(y) \quad (3.42)$$

where $\mathbf{I}$ is the identity matrix.

Here we want to solve the temporal stability. In the temporal framework of the linear stability analysis, temporal eigenvalues, ω_e are sought for a given (real) wavenumber, k . When the wavenumber k is given real, the complex solution for ω_e are called the temporal modes or branches (Godréche, 1998).

$$\omega_e \equiv \omega_r + i\omega_i \quad (3.43)$$

The possible eigenmodes are obtained for each real wave number, k and range of the parameters of interest.

$$\bar{\mathbf{a}}(x, y, t) = \hat{\mathbf{a}}_e(y) e^{i(kx - \omega_e t)} \quad (3.44)$$

where $\hat{\mathbf{a}}_e(y)$ is eigenvector corresponding to the eigenvalue, ω_e .

The freely evolving waves are spatially periodic disturbances of infinite spatial extent which travel with a phase velocity, $c_r \equiv \omega_r / k$ and grow or decrease in amplitude with a temporal growth rate, ω_i . The system is considered to be linearly unstable to infinitesimal disturbances for $\omega_i > 0$. The stability regimes can be distinguished as follows:

$$\omega_i \begin{cases} > 0 \longrightarrow \text{instability} \\ = 0 \longrightarrow \text{neutral} \\ < 0 \longrightarrow \text{stability} \end{cases} \quad (3.45)$$

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The boundary conditions are applied to the temporal stability analysis at the walls $y = \pm 1$,

$$\frac{\partial \bar{u}}{\partial y} = 0 \quad (3.46(a))$$

$$\bar{v} = 0 \quad (3.46(b))$$

$$\frac{\partial \bar{c}}{\partial y} = 0 \quad (3.46(c))$$

$$\frac{\partial \bar{\phi}}{\partial y} = 0 \quad (3.46(d))$$

Boundary condition (3.46(a)) is the approximation for the Couette flow. Boundary condition (3.46(b)) assumes a stationary wall. Boundary conditions (3.46(c)) and (3.46(d)) are zero mass and electric fluxes at the walls.

The system was solved by using a pseudo spectral method (Trefethen, 2001; Weideman and Reddy, 2000). Eigenvalue convergence was obtained using 20 points and validated using 40 points expansion.

3.3.1.5 Base State

To simplify the problem the base state is assumed as one-dimensional parallel flows with the flow conditions denoted by $(u_0(y, t), v_0(y, t), w_0(y, t), P_0(y, t), c_0(y, t), \phi_0(y, t))$. Subscript '0' denotes the base state. A linear stability analysis is performed on this base state. In carrying out a linear stability analysis, small disturbances are introduced to the system and their evolution is analyzed to determine if the disturbances grow (are unstable), decay (are stable), or remain constant (neutrally stable) with time.

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In the base state, the concentration is assumed as a function of y and t only and obeys the simple diffusion equation and Neumann boundary condition.

$$Pe \frac{\partial c_0}{\partial t} = \frac{\partial^2 c_0}{\partial y^2} \quad (3.47(a))$$

$$\left. \frac{\partial c_0}{\partial y} \right|_{y=\pm 1} = 0 \quad (3.47(b))$$

To determine $c_0(y, t)$, we first solve an initial value problem where the concentration satisfies the initial condition. The resulting concentration profile is then treated as a base state to the linear instability analysis. The diffusion time is equal to advection time of the fluid as it comes from the channel inlet to the viewing area (Chen *et al.*, 2005). Base state solution for the concentration is

$$c_0(y, t) = \begin{cases} \left[\frac{\gamma-1}{\gamma+1} \sum_{n=0}^{\infty} \left[\frac{2(-1)^n}{(2n+1)\pi} e^{-\frac{\left(\frac{2n+1}{2}\right)^2 \pi^2 t}{Pe}} \cos\left(\frac{2n+1}{2}\pi(y-1)\right) \right] + 1 \right] & 0 \leq y \leq 1 \\ \left[\frac{1-\gamma}{1+\gamma} \sum_{n=0}^{\infty} \left[\frac{2(-1)^n}{(2n+1)\pi} e^{-\frac{\left(\frac{2n+1}{2}\right)^2 \pi^2 t}{Pe}} \cos\left(\frac{2n+1}{2}\pi(y+1)\right) \right] + 1 \right] & -1 \leq y \leq 0 \end{cases} \quad (3.48)$$

Where $\gamma = \frac{c_h}{c_l}$ is the concentration ratio.

The base velocity u_0 varies to the different base state of the concentration if $n \neq 0$. u_0 must be a solution to the Navier-Stokes equation. The difference in the concentration leads to different electroosmotic velocities at the upper and lower boundaries of the channel. We

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choose the base flow field as Couette flow. The base state applied electric field E_0 is directed along the streamwise direction.

3.3.2 Results for Linear Stability Analysis

3.3.2.1 Temporal Instability

Table 3.1 Parameters for linear stability analysis and numerical simulation

Symbol	Description	Value
h	half height	5.5×10^{-6} m
w	half width	7.8×10^{-5} m
ρ	density	1.0×10^{-3} kg m ⁻³
μ	dynamic viscosity	1.0×10^{-3} kg m ⁻¹ s ⁻¹
ε	permittivity	6.9×10^{-10} CV ⁻¹ m ⁻¹
n	correlation coefficient	0, -1/3, -1/2
ζ_r	reference zeta potential	1.4×10^{-2} V
m_+	molar conductivity	5×10^{-3} Sm ² mol ⁻¹
m_-	molar conductivity	2.7×10^{-3} Sm ² mol ⁻¹
c_r	reference concentration	5.5 mM

In this section, we chose the set of experimental parameters (Table 3.1) reported by Chen *et al.* (2005) to investigate the electrokinetic instability. The permittivity, viscosity and density of dilute Borate solutions were taken to be those of pure water. The molar conductivity of Na^+ is 5×10^{-3} Sm²mol⁻¹ and the molar conductivity of $B(OH)_4^-$ is 2.7×10^{-3} Sm²mol⁻¹. The ionic diffusivities were obtained from $m_i = \frac{D_i}{RT}$. The effective diffusivity was obtained from Eq. (3.15). The concentration ratio is $\gamma = \frac{c_h}{c_l} = 10$. In this

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case zeta potential is assumed to be uniform. Unless specified otherwise, the uniform base state velocity of the different concentration $n = 0$ is used in the thesis.

Figure 3.2 shows a contour plot of temporal growth rate (ω_i) versus wave number (k) and applied electric field (E_0). The neutral stability curve corresponds to a growth rate of 0. For the region above this neutral stability curve, the flow is unstable, while flow is stable for the region below this curve. The critical electric field can be determined from the minimal value of E_0 on the neutral stability curve. The electric field for the onset of instability is approximately 0.22 kV/cm. In Chen’s experiment, the threshold E_0 is 0.5 ± 0.1 kV/cm and predicted theoretical E_0 is 0.15 kV/cm.

Figure 3.2 Contour plot of growth rate (ω_i) versus wave number (k) and applied electric field (E_0).

The ratio of the concentration between two streams is 10.

The magnitude of the zeta potential, $\zeta_r = \zeta_0$.

3.3.2.2 Comparison between with Diffusion Current and without Diffusion Current

In section 3.2.1.3, the current density is made up of contributions from electromigration (conduction) current under the action of electric field and the diffusion current due to the concentration gradient in Eq. (3.19).

Fig. 3.3 shows a contour plot of the growth rate (ω_i) versus wave number (k) and applied electric field (E_0) for 2 cases: (a) without the diffusion current term in Eq. (3.179) and (b) with the diffusion current term in Eq. (3.19). The ratio of the concentration between two streams is 10. The correlation coefficient is $n = -1/3$. The critical electric field for case (b) is a little smaller than case (a). The result shows that the effects of the diffusion current term is negligible compared to the conduction current.

Figure 3.3 Contour plot of growth rate (ω_i) versus wave number (k) and applied electric field (E_0).
The correlation coefficient is $n = -1/3$.

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Eq. (3.39(e)) is the dimensionless depth-averaged disturbance equation from the conservation of the charge. $G_2 \left(\frac{\partial^2 \bar{c}}{\partial x^2} + \frac{\partial^2 \bar{c}}{\partial y^2} \right)$ represents the effect of the diffusion current due to the concentration gradient, while the L.H.S. of Eq. (3.39(e)) represents the influence of the conduction current under the applied electric field. $G_2 = \frac{M}{wE_0}$ is a dimensionless parameter which is inversely proportional to the electric field, E_0 . As increasing the applied electric field, $G_2 = \frac{M}{wE_0} \sim 10^{-2}$. Thus, the diffusion current term trail off and the electromigration effect dominates with increasing the applied electric field.

3.3.2.3 Effect of the Correlation Coefficient

Zeta potential is a property of the surface material that is influenced by a number of factors: electrolyte concentration, pH value of the solution and level of surface adsorption. To simplify the analysis, the wall zeta potential is assumed to relate to ionic concentration by $\frac{\zeta}{\zeta_r} = \left(\frac{c}{c_r} \right)^n$, where n is a correlation coefficient. Fig. 3.4 presents neutral curves for different correlation coefficients with $n = 0$ (uniform electroosmotic flow), $n = -1/2$ and $n = -1/3$. These coefficients ($n = -1/3, -1/2$) correspond to the non-uniform electroosmotic velocities. The figure shows that the onset of instability for $n = 0$, $n = -1/3$ and $n = -1/2$ occurs at wave numbers, $k = 0.08$, $k = 0.9$ and $k = 1$, respectively. The corresponding critical electric fields, E_0 , are 0.22, 0.26 and 0.30 KV/cm, respectively. The results show that for uniform electroosmotic flow, the onset of instability occurs at a relatively low

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wave number ($k = 0.08$) corresponding to a long wavelength disturbances. Since the velocity gradient for $n = -1/2$ is larger than $n = -1/3$ and $n = 0$, the critical electric field increases from 0.22 ($n = 0$) to 0.30 KV/cm ($n = -1/2$) . These results demonstrate that the velocity gradient can be a stabilizing effect. Thus, critical electric field needed for the onset of instability is the lowest for a uniform base state of electroosmotic velocity.

Figure 3.4 Comparison of the contour plot of neutral stability ($\omega_i=0$) for various correlation coefficients n .

3.3.2.4 Effect of the Different Concentration Ratio

Fig. 3.5 shows the dependence of the critical electric field strength (E_0) as a function of

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the concentration ratio, γ . As the concentration ratio increases, E_0 decreases dramatically and approaches an asymptotic limit. The critical field exhibits strong dependence at low concentration ratios when the concentration ratio is less than 5, but a weaker dependence at high concentration ratios.

Figure 3.5 Critical electric field for different concentration ratios

3.3.2.5 Effect of the Zeta Potential

Figs. 3.6 and 3.7 show a contour plot of growth rate versus wave number and electric field for zeta potentials $\zeta_r = 5\zeta_0$ and $\zeta_r = 10\zeta_0$, respectively, while Fig. 3.2 shows a contour plot of the growth rate versus wave number and electric field for $\zeta_r = \zeta_0$. The results indicate that the critical electric field and the onset of instability remain unchanged for increasing zeta potential. Growth rate varies with zeta potential for a given electric field and wave number. An example, the growth rates at $E_0 = 0.4$ kV/cm with the

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Figure 3.6 Contour plot of growth rate (ω_i) versus wave number (k) and applied electric field (E_0).
The magnitude of the zeta potential, $\zeta_r = 5\zeta_0$.

Figure 3.7 Contour plot of growth rate (ω_i) versus wave number (k) and applied electric field (E_0).
The magnitude of the zeta potential, $\zeta_r = 10\zeta_0$.

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wave number $k = 1.5$ are 0.08, 0.016 and 0.008 for $\zeta_r = \zeta_0, 5\zeta_0, 10\zeta_0$ respectively. The magnitude of zeta potential influence only the growth rate of the disturbances, growth rate decreases with the increase of zeta potential. When the zeta potential increases from $\zeta_r = 5\zeta_0$ to $\zeta_r = 10\zeta_0$, the magnitude of the electroosmotic flow velocity increases linearly. Thus, the major role of electroosmotic flow is to convect the perturbation, but it can't enhance the mixing of the electrolyte of different concentrations.

3.3.2.6 Effect of the Diffusion Coefficient

Figs. 3.8 and 3.9 show a contour plot of growth rate versus wave number and electric field for $D = 1.5D_0$ and $D = 3D_0$ respectively, while Fig. 3.2 shows a contour plot of the growth rate for $D = D_0$. The critical electric field for the diffusion coefficient, $D = D_0$, $D = 1.5D_0$ and $D = 3D_0$ are 0.22 kV/cm, 0.28 kV/cm and 0.38kV/cm respectively. As comparing the contour of growth rate, the results indicate that growth rate of the disturbances decreases with the increase of the diffusion coefficient. The two streams will be significantly mixed via molecular diffusion and the flow is more stable for increased diffusion coefficient. For a given concentration gradient, the critical electric field is higher for larger values of the diffusion coefficient. The results demonstrate that diffusion coefficient is a stabilizing effect.

Due to the low Reynolds number region in the microfluidic devices, species mixing is strongly diffusion dominated; hence a larger diffusion coefficient is preferred for efficient mixing. However, the onset and development of the electrokinetic instability is hindered

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by a larger diffusion coefficient.

Figure 3.8 Contour plot of growth rate (ω_i) versus wave number (k) and applied electric field (E_0).

The diffusion coefficient is $D = 1.5D_0$.

Figure 3.9 Contour plot of growth rate (ω_i) versus wave number (k) and applied electric field (E_0).

The diffusion coefficient is $D = 3D_0$.

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3.3.2.7 Electrokinetic Instability Mechanism

The contour plot of the concentration, charge density, electric field, u component velocity, v component velocity and streamline perturbations are shown in Fig 3.10 (a), (c), (d), (e), (f) and (g) respectively at an electric field $E_0 = 0.50$ kV/cm and a wave number $k = 1.5$ with a uniform base state of electroosmotic flow. The contour of concentration perturbation (Fig 3.10 (a)), charge density (Fig 3.10 (c)) and electric field perturbation (Fig 3.10 (d)) exhibit a cellular pattern. The “ H ” and “ L ” signs indicate the local maxima and minima points of the cell which alternate in the x -direction. The concentration perturbation affects the electric field distribution by the charge conservation equation (3.37(e)). In this simulation case, the results show that within a cellular structure, a “ H ” concentration perturbation results in a “ L ” electric field perturbation and vice versa. This perturbed electric field results in a perturbation in the charge density of the form, $\bar{\rho}_e = -\epsilon \nabla^2 \bar{\phi}$. Fig 3.10(c) shows the contour plot of charge density perturbation. Additional positive and negative charges are induced periodically by the perturbed electric field. These induced electrical charges interact with the external applied electric field generate an electric body force and produce a rotating cellular flow motion as showed in Fig 3.10(g). This rotating cellular flow further alternates the concentration field through the convection diffusion equations and lead to the growth and propagation of instability waves.

Fig 3.10(b) shows the contour plot of the fluid concentration distribution along the micro-channel by superposed the base state on the disturbance concentration. The instability produces a periodic sinusoidal concentration wave along the stream. In an attempt to

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explain the physics of electrokinetic instability, one cycle of periodic from $a-o-b$ and $b-o-c$ is analyzed. In Fig 3.10(a,b), fluid concentration is highly perturbed at the interface of the adjacent streams due to the large concentration gradient. As the concentration field is perturbed, concentration gradient at the bulk mixing layer $a-o-b$, $\partial c / \partial x < 0$ while $\partial c / \partial x > 0$ at the bulk mixing layer $b-o-c$. From Eq. (3.19), the charge accumulation is the direct result of the charge conservation. The charge density is given as: $\rho_e = (-\varepsilon M \nabla^2 c - \varepsilon \nabla c \cdot E) / c$, hence charge accumulation is directly linked to the ionic concentration gradient. The first and second terms on the R.H.S. of ρ_e represent the molecular diffusion and the electromigration of charges, respectively. Since the effect of electro-migration dominates the molecular diffusion, charge accumulation in the bulk mixing layer $a-o-b$ is positive, $\rho_e > 0$ whereas in the bulk mixing layer $b-o-c$ is negative, $\rho_e < 0$. As a result positive and negative charges are induced periodically in Fig 3.10(c). These induced electrical charges interact with the external applied electric field and generate an electric body force $F \approx \rho_e \cdot E$ which leads to velocity perturbation. The strength of the velocity perturbation depends on the sign and magnitude of the induced charges and the applied electric field. Figs 3.10(e,f) show the u and v components of the perturbed velocity. It is noted that $\bar{v}$ perturbs upward in region $o-b-o$ and downward in region $o-c-o$. This regular perturbed $\bar{u}$ and $\bar{v}$ lead to the rotating cellular flow of successive positive and negative vortex as showed in Fig 3.10(g) which stretches and folds material lines for rapid mixing.

The contour plot of the concentration, charge density, electric field, u component

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velocity, v component velocity and streamline perturbations are shown in Fig 3.11 (a), (c), (d), (e), (f) and (g) respectively at an electric field $E_0 = 0.50$ kV/cm and a wave number $k = 1.5$ with a non-uniform base state of electroosmotic flow ($n=-1/2$). When $n=-1/2$, the velocity profile of two electrolytes are nonuniform. Stream c_l flows faster than c_h , hence the results of the perturbation variables show a leftward slanting cells.

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Figure 3.10 Contour plot of concentration, charge density, electric field , u component velocity, v component velocity and streamline perturbations are shown in (a), (c), (d), (e), (f) and (g) respectively at an electric field $E_0 = 0.50$ kV/cm , wave number $k = 1.5$ and a uniform base state of electroosmotic flow ($n=0$). The contour of the fluid concentration distributions along the microchannel by superposed the base state on the disturbance concentration are shown in (b) $\bar{c} + \bar{c}_0$.

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Figure 3.11 Contour plot of the concentration, charge density, electric field, u component velocity, v component velocity and streamline perturbations are shown in (a), (c), (d), (e), (f) and (g) respectively at an electric field $E_0 = 0.50$ kV/cm, wave number $k = 1.5$ and a nonuniform base state of electroosmotic flow ($n = -1/2$). The contour of the fluid concentration distributions along the microchannel by superposed the base state on the disturbance concentration are shown in (b) $\tilde{c} + \bar{c}_0$.

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3.4 Nonlinear Numerical Simulation

In the linear stability analysis, the governing equations are linearized by neglecting the higher power and product terms. In view of the linearized approximation, well organized periodic flow structure is predicted, such as the regular cellular concentration contour and the regular rotating cellular flow in Fig. 3.10. To obtain a detailed time evolution of the instability, it is necessary to perform the numerical analysis on the flow.

3.4.1 Simplifications and Numerical Method

The governing equations (3.23) on continuity, momentum, species and charge conservation for incompressible, isothermal, electrokinetic microflows of dilute binary electrolyte are dimensionlized by the following parameters:

$$\begin{aligned}
 \bar{x} &= \frac{x}{w} & \bar{y} &= \frac{y}{w} & \bar{t} &= \frac{t}{w/V_{EV}} & \bar{c} &= \frac{c}{c_r} \\
 \bar{u} &= \frac{u}{V_{EV}} & \bar{v} &= \frac{v}{V_{EV}} & \bar{\phi} &= \frac{\phi}{E_0 w} & \bar{P} &= \frac{P}{\rho V_{EV}^2} \\
 Pe &= \frac{w V_{EV}}{D_{eq}} & Re &= \frac{\rho V_{EV} w}{\mu} & G_1 &= \frac{\varepsilon E_0^2}{\rho V_{EV}} & G_2 &= \frac{M}{w E_0}
 \end{aligned} \tag{3.49}$$

Thus, the governing equations in dimensionless form are

$$\frac{\partial \bar{u}}{\partial \bar{x}} + \frac{\partial \bar{v}}{\partial \bar{y}} = 0 \tag{3.50(a)}$$

$$\frac{\partial \bar{u}}{\partial \bar{t}} + \bar{u} \frac{\partial \bar{u}}{\partial \bar{x}} + \bar{v} \frac{\partial \bar{u}}{\partial \bar{y}} = -\frac{\partial \bar{P}}{\partial \bar{x}} + \frac{1}{Re} \left(\frac{\partial^2 \bar{u}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{u}}{\partial \bar{y}^2} \right) - G_1 \left(\frac{\partial^2 \bar{\phi}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{\phi}}{\partial \bar{y}^2} \right) \tag{3.50(b)}$$

$$\frac{\partial \bar{v}}{\partial \bar{t}} + \bar{u} \frac{\partial \bar{v}}{\partial \bar{x}} + \bar{v} \frac{\partial \bar{v}}{\partial \bar{y}} = -\frac{\partial \bar{P}}{\partial \bar{y}} + \frac{1}{Re} \left(\frac{\partial^2 \bar{v}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{v}}{\partial \bar{y}^2} \right) \tag{3.50(c)}$$

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$$\frac{\partial \bar{c}}{\partial t} + \bar{u} \frac{\partial \bar{c}}{\partial x} + \bar{v} \frac{\partial \bar{c}}{\partial y} = \frac{1}{Pe} \left(\frac{\partial^2 \bar{c}}{\partial x^2} + \frac{\partial^2 \bar{c}}{\partial y^2} \right) \quad (3.50(d))$$

$$\nabla \cdot (\bar{c} \nabla \bar{\phi}) = G_2 \left(\frac{\partial^2 \bar{c}}{\partial x^2} + \frac{\partial^2 \bar{c}}{\partial y^2} \right) \quad (3.50(e))$$

Governing Eqs. (3.50) are solved by the control volume method. The equations are discretized using the control volume method, and the staggered grid system is utilized. The power-law of Patankar (1980) is used to model the combined convection-diffusion effect. The Crank-Nicolson time scheme is used to discretize the transient term. The resulting algebraic equations are solved using the TriDiagonal Matrix Algorithm.

3.4.2 Validation for the Numerical Method

Fig. 3.12 shows the computational domain and mesh for 2-D laminar incompressible flow around a square cylinder placed in a uniform stream. The grid is finer near the surfaces of the square cylinder to better resolve the gradients near the wall. Fig. 3.13 shows the lift and drag coefficients versus time for $Re = 100$ for three different grids: fine-grid 145×100 , intermediate-grid 90×80 and coarse-grid 60×50 . The Strouhal number is 0.12056, 0.12186 and 0.13354 for fine, intermediate and coarse grids respectively, which agrees well with the experimental value of 0.118 reported by Okajima (1982) and Bejan (1982). The results show that the intermediate grid is sufficiently fine for the simulation. Fig. 3.14 shows instantaneous streamlines during one cycle of periodic unsteady flow behind a square cylinder. The results confirmed that the numerical code is capable to capture the vortex shedding effect behind a square cylinder.

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Figure 3.12 Computational domain and mesh for flow around a square cylinder

Figure 3.13 Comparison of the lift and drag coefficient versus time for three grids

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Figure 3.14 Instantaneous streamlines during one cycle of periodic unsteady flow behind a square cylinder

3.4.3 Results for Nonlinear Simulation

The channel geometry and flow parameters for the nonlinear simulation were chosen to be the same as those of the linear stability analysis as shown in Table 3.1.

Fig. 3.15 shows the schematic of the piecewise-uniform fitted mesh in y -direction for the simulation of electrokinetic instability. The grid is finer at the interface of the two streams and the boundary to better resolve the gradients.

Figure 3.15 Schematic of the piecewise-uniform fitted mesh in y -direction for the electrokinetic instability

Fig. 3.16 show the nonlinear evolution of the concentration field for various electric fields, $E_0 = 0.1, 0.25, 0.5, 1.00$ kV/cm. The electrokinetic instability phenomenon begins at the electric field $E_0 = 0.25$ kV/cm (Fig 3.16(b)). Figure 3.16(a) shows that there is no electrokinetic instability at $E_0 = 0.1$ kV/cm. The flow is stable and the concentration distribution is governed by molecular diffusion at $E_0 = 0.1$ kV/cm. At the electric field

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($E_0 = 0.25$ kV/cm, Fig 3.16(b)), from 0.1 s to 0.2 s, a very slight disturbance appears at the upstream of the channel, the disturbance typically originates at the interface and grows as they advect downstream.

Fig 3.16(c,d) show the nonlinear evolution of the instability at electric fields, $E_0 = 0.5$ and 1.00 kV/cm. In Fig 3.16 (c,d) from 0.05 s to 0.2 s, we see that small amplitude waves observed at $t = 0.05$ s grow rapidly and form alternating flow structure which stretches and folds materials line as they advect downstream. Electrolytes are mixed rapidly due to flow instability. The results indicate that the interface of adjacent streams is strongly disturbed due to the high concentration gradient. The concentration profiles exhibit complex wave structures rather than the simple sinuous patterns. At higher applied electric, the structure becomes chaotic flow. The numerical model reproduces important flow features observed in Chen *et al.* (2005)'s experiments such as the transverse growth of a wave pattern in the interface, and the roll up of wave structures observed.

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(c) $E_0 = 0.5 \text{ kV/cm}$

(d) $E_0 = 1.0 \text{ kV/cm}$

Figure 3.16 The snapshots of the concentration at the various instances for different electric fields.

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Fig 3.17 shows the mixing efficiency for four electric fields at $t = 0.20\text{ s}$. When the electric field $E_0 = 0.1\text{ kV/cm}$ is smaller than the critical one, mixing is achieved solely through the diffusion of the inhomogeneous streams, and hence the maximum mixing efficiency attains a value of 20% at $t = 0.20\text{ s}$. At a higher electric field, the mixing efficiency has an undulating form. Some places reach local maximum mixing efficiency and vice versa which alternate in the x-direction. The mixing efficiency is enhanced by the electrokinetic instability mixing compared to the sole diffusion.

Figure 3.17 Mixing Efficiency for four electric fields at $t = 0.20\text{ s}$ along the mixing channel length

Figure 3.18(a) show the calculated concentration distribution for $E_0 = 0.35\text{ kV/cm}$, $Re = 20.57$, $Pe = 22032.36$. Unsteady waves are observed continuously rolling up or down at the downstream distance 2, 5, 8, 12 and 15. The amplitude of the waves grows as it is advected downstream. The simulated interfacial waves resemble those observed in the experimental (Chen *et al.* (2005)).

Figure 3.18(b) shows that the calculated electric field distribution exhibits a cellular

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pattern which alternate in the x -direction. Figure 3.18(c) shows the distribution of the positive and negative charges accumulate near the interface of the high and low concentration regions.

Figure 3.18(d) and 3.18(e) show the calculated u velocity and streamline. We can see strong vortices at the downstream distance 4, 7, 10 and 12.

Figure 3.18 Numerical results at an instant for $E_0 = 0.35$ kV/cm .

3.5 Summary

The linear stability analysis is presented for the electrokinetic instability mixing. The instability mechanism is revealed through parametric variations:

1. In the charge conservation equation, the effect of diffusion current term is negligible compared to the conduction current.
2. The velocity gradient is a stabilizing effect. The critical electric field strength needed for the onset of instability is the lowest for a uniform base state of electroosmotic velocity.
3. Applied electric field, E_0 decreases dramatically and approaches an asymptotic limit with increasing the concentration ratio, γ .
4. The diffusion coefficient is a stabilizing effect. For a given concentration gradient, the critical electric field is higher for larger values of the diffusion coefficient.
5. The contour of concentration perturbation (Fig. 3.10 (a)), charge density (Fig. 3.10 (c)) and electric field perturbation (Fig. 3.10 (d)) exhibit a cellular pattern. The actual concentration (Fig. 3.10 (b)) shows a periodic sinusoidal concentration wave along the stream. The concentration perturbation affects the electric field distribution. This perturbed electric field results in a perturbation in the charge density. The induced electrical charges interact with the external applied electric field generate an electric body force and produce a rotating cellular flow motion. The rotating cellular flow further alternates the concentration field through the convection diffusion equations and lead to the growth and propagation of instability waves.

The control volume numerical nonlinear simulation is developed to obtain a detailed time

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evolution of the instability. The results show that the interface of adjacent streams is strongly disturbed due to the high concentration gradient. The concentration profiles exhibit complex wave structures. At higher applied electric field, the structure becomes chaotic flow.

CHAPTER 4

Electroosmotic flow in irregularly shaped microchannels

4.1 Introduction

The literature survey in section 1.4.2 shows that so far all the reported work focuses on the electroosmotic flow in regularly shaped microchannels. In an attempt to develop an electrokinetic actuator using the concept of electroosmotic flow in closed-end packed capillaries, this section presents semi-analytical solutions for electroosmotic driven flow in open-end and closed-end irregularly shaped microchannels.

A novel concept on electrokinetic actuator is proposed in Fig 4.1. The electrokinetic actuator consists of three main components: an electroosmotic component, a hydraulic component and an actuator component. In the electroosmotic component, we propose the use of frequency-dependent excitation electric field over non-conductive closed-end capillaries. The capillaries are filled with an aqueous liquid. Since the capillaries are sealed, there will be no net flow, and hence a back pressure will be built up. This back pressure can be converted to force for actuation. For practical applications, if a high force is required, hundreds or thousands of microcapillaries can be bundled together to provide large cross section areas and hence a large force.

Figure 4.1 Schematic diagram of the electroosmotic flow actuator

The system aims to tap the pressure generated by the electroosmotic system to operate actuators. The high pressure at one end is utilized to set the electroosmotic piston in motion. The hydraulic component serves to amplify the displacement of the piston as the displacement of the electroosmotic piston is very minute. The properties of the system to be investigated include the pressure variations, displacement and oscillating frequency of the pistons that the electroosmotic component can induce.

The electroosmotic component can be designed in various ways as shown in Fig 4.2, such as rectangular-microchannel-packed-tube or circular-microchannel-packed-tube. We focus on the investigation of fluid flow characterizations within an electroosmotic component of the electrokinetic actuator. In the design of electrokinetic actuator, it is possible for fluid to flow within or outside the channels. The literature survey shows that so far there is no reported work on the electroosmotic flow in irregularly shaped microchannels. The comparison between the flow inside and outside the channels is not known yet. This work focuses on the investigation of the EOF within the irregularly

shaped microchannels.

Figure 4.2 Schematic of the electroosmotic component designs

Fig. 4.3 shows the schematic of the packed capillaries. The flow can be modeled as unidirectional flow through a bundle of small parallel packed capillaries of radius, R_0 . In this design, the fluid can flow inside the packed capillaries, which means flows in the circular capillaries. Fluid can also flow outside the packed capillaries, which means flows in star point family microchannels.

Figure 4.3 Schematic of the packed capillaries

4.2 Steady State Electroosmotic Flow

Here, we consider the flow outside the packed capillaries, which means fluid flow through a four-point-star microchannel as shown in Fig. 4.4(a). The channel wall is assumed to be uniformly charged with a zeta potential, ζ_0 . When an external electric field, E_0 , is applied along the axial direction of the channel, the liquid moves along the channel as a result of the interaction between the net charge density in the EDL and the applied electric field. To analyze the flow, a coordinate axis is placed at the origin point, O. Due to symmetry, only one-eighth of the cross section of the four-point-star microchannel is analyzed, as shown in Fig. 4.4(b). EDL forms along the arc wall DA and the no-slip condition is applied along the arc DA.

Fig. 4.4(a)

Fig. 4.4(b)

Figure 4.4 (a) Cross section of the four-point-star microchannel
(b) One eighth of the four-point-star microchannel

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4.2.1 Electrical Potential Distribution

According to the theory of electrostatics, the relationship between the electric potential distribution ϕ and the net charge density per unit volume ρ_e at any point in the solution is described by the Poisson equation given in Eq. (4.1).

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = -\frac{\rho_e}{\epsilon_0 \epsilon_r} \quad (4.1)$$

where ϵ_0 is the permittivity of vacuum and ϵ_r is the dielectric constant of the fluid.

For a microchannel of length large compared with its packed capillary radius, R_0 (Probstein, 1994), the term $\partial^2 \phi / \partial z^2$ may be neglected, to give

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = -\frac{\rho_e}{\epsilon_0 \epsilon_r} \quad (4.2)$$

It is convenient to divide the electric potential into two parts: the applied electric potential, $\phi(z)$ and induced electric potential, $\psi(x, y)$.

$$\phi(x, y, z) = \phi(z) + \psi(x, y) \quad (4.3)$$

So Poisson's equation can be written as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{\rho_e}{\epsilon_0 \epsilon_r} \quad (4.4)$$

In a fully developed hydrodynamic state, the net charge density in the diffuse layer obeys the Boltzmann distribution:

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$$\rho_e = -2z_v e n_0 \sinh\left(\frac{z_v e \psi}{k_b T}\right) \quad (4.5)$$

where n_0 and z_v are bulk concentration and valence of type- i ions, respectively, e is the elementary charge, k_b is the Boltzmann constant, and T is the absolute temperature.

Substituting Eq. (4.5) into Eq. (4.4) leads to the Poisson-Boltzmann equation in Eq. (4.6).

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{2z_v e n_0}{\epsilon_r \epsilon_0} \sinh\left(\frac{z_v e \psi}{k_b T}\right) \quad (4.6)$$

By defining the *Debye-Hückel* parameter $\kappa = \left(2z_v^2 e^2 n_0 / \epsilon_r \epsilon_0 k_b T\right)^{1/2}$ and the hydraulic diameter of the microchannel as $D_h = \frac{2(4-\pi)R_0}{\pi}$ and introducing the dimensionless groups $\bar{x} = x / D_h$, $\bar{y} = y / D_h$, $K = \kappa D_h$ and $\bar{\psi} = z_v e \psi / k_b T$, the above equation can be non-dimensionalized as:

$$\frac{\partial^2 \bar{\psi}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{\psi}}{\partial \bar{y}^2} = K^2 \sinh(\bar{\psi}) \quad (4.7)$$

where κ has the unit of m^{-1} and $1/\kappa$ is referred to the characteristic thickness of the EDL.

In the one eighth of the four-point-star microchannel, due to symmetry of the EDL field, Eq. (4.7) is subjected to the following boundary conditions, as shown in figure 4.4(b):

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$$\begin{aligned}
 \bar{\psi} &= \bar{\zeta}_0 && \text{on arc } \widehat{DA} \\
 \frac{\partial \bar{\psi}}{\partial y} &= 0 && \text{along OD} \\
 \frac{\partial \bar{\psi}}{\partial x} - \frac{\partial \bar{\psi}}{\partial y} &= 0 && \text{along OA}
 \end{aligned} \tag{4.8}$$

where the non-dimensional zeta potential is defined as $\bar{\zeta}_0 = \frac{z_v e \zeta_0}{k_B T}$.

The finite element method (FEM) is applied to solve Eq. (4.7) because of the complex geometry configuration of the star shaped microchannel. The Poisson-Blotzmann Eq. (4.7) with the boundary conditions Eq. (4.8) can be written in Garlerkin residual integral with respect to the space coordinates.

Once the electrical potential distribution is known, the ionic net charge density can be obtained from Eq. (4.5). This local net charge density is required to determine the electrostatic force caused by the presence of EDL field. Such an electrostatic force is considered as an additional body force exerting on the electrolyte to modify the conventional Poiseuille flow equation, which will be discussed in the following sections.

4.2.2 Electroosmotic Flow Field in a closed-end Microchannel

The Navier-Stokes equation represents the fluid flow in general cases. However, it has to be modified to include the electric force generated by the interaction between the EDL and the applied electrical field. The equation of motion for an incompressible

Newtonian liquid has been modified and it becomes

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \cdot \nabla) \vec{V} = -\nabla \bar{P} + \vec{F} + \mu \nabla^2 \vec{V} \quad (4.9)$$

where $\vec{V}$ is the velocity vector, ρ is the density of the fluid and, μ is the dynamic viscosity of the fluid. If the gravity effect is negligible, the force $\vec{F}$ is caused only by the action of the applied electrical field E_0 on the net charge density ρ_e in the EDL regions of the electrolyte, as

$$F_z = E_0 \rho_e \quad (4.10)$$

To evaluate the electrokinetic effects, a simple Newtonian flow with a constant viscosity is assumed, which is independent of shear rate and the local electric field strength. For a steady, fully developed, laminar flow, the components of velocity $\vec{V}$ satisfy $u_z = u(r, \theta)$ and $u_r = u_\theta = 0$ in terms of cylindrical coordinates. Thus both the time term $\frac{\partial \vec{V}}{\partial t}$ and inertia term $(\vec{V} \cdot \nabla) \vec{V}$ vanish. The hydraulic pressure $\bar{P}$ is a function of z only and the pressure gradient $\frac{dP}{dz}$ is a constant. With these considerations, Eq. (4.9) is reduced in the cylindrical coordinates as shown in Eq. (4.11).

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} + \frac{1}{\mu} \left(-\frac{dP}{dz} + E_0 \rho_e \right) = 0 \quad (4.11)$$

For the star point microchannels, the Poisson-Boltzmann equation will be presented in the cylindrical coordinate. The electric potential distribution varies in the radial and

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angular directions and the two dimensional formulation is given in Eq. (4.12).

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \theta^2} = -\frac{\rho_e(r, \theta)}{\varepsilon_0 \varepsilon_r} \quad (4.12)$$

Substitute Eq. (4.12) into Eq. (4.11), we get Eq. (4.13):

$$\frac{\partial^2 (u - E_0 \varepsilon_0 \varepsilon_r \psi / \mu)}{\partial r^2} + \frac{1}{r} \frac{\partial (u - E_0 \varepsilon_0 \varepsilon_r \psi / \mu)}{\partial r} + \frac{1}{r^2} \frac{\partial^2 (u - E_0 \varepsilon_0 \varepsilon_r \psi / \mu)}{\partial \theta^2} + \frac{1}{\mu} \left(-\frac{dP}{dz} \right) = 0 \quad (4.13)$$

Introduce $S = \frac{1}{\mu} \left(-\frac{dP}{dz} \right)$ and $v(r, \theta) = u(r, \theta) - E_0 \varepsilon_0 \varepsilon_r \psi(r, \theta) / \mu + \frac{Sr^2}{4}$, Eq. (4.13) is

transformed into a more conveniently solvable form:

$$\frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} + \frac{1}{r^2} \frac{\partial^2 v}{\partial \theta^2} = 0 \quad (4.14)$$

Hence, the finite-series solutions of the velocity field can be derived from the method of separation of variables (Shih, 1967).

$$u(r, \theta) = E_0 \varepsilon_0 \varepsilon_r \psi(r, \theta) / \mu - \frac{Sr^2}{4} + A'_0 + \sum_n A'_n r^n \cos n\theta \quad (4.15)$$

The characteristic numbers must be integers and satisfy

$$n = m\pi / \beta, m = 1, 2, 3 \dots \quad (4.16)$$

where β is the angle between the two intersecting lines of symmetry, $\beta = \frac{\pi}{4}$, as shown in Fig. 4.4(b).

The no slip condition along the microchannel wall DA remains to be imposed. The

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boundary point D at $(r_0, 0)$ provides $u(r_0, 0) = 0$, $\psi(r_0, 0) = \zeta_0$. Hence, Eq. (4.15)

yields:

$$A'_0 = -E_0 \varepsilon_0 \varepsilon_r \zeta_0 / \mu + \frac{S r_0^2}{4} - \sum_n A'_n r_0^n \quad (4.17)$$

Substituting Eq. (4.17) back into Eq. (4.15), one obtains:

$$u(r, \theta) = \frac{E_0 \varepsilon_0 \varepsilon_r}{\mu} [\psi(r, \theta) - \zeta_0] + \frac{S}{4} \left[(r_0^2 - r^2) - \sum_n A'_n (r_0^n - r^n \cos n\theta) \right] \quad (4.18)$$

Eq. (4.16) gives $n = 4m$, and so Eq. (4.18) becomes

$$u(R, \theta) = \frac{E_0 \varepsilon_0 \varepsilon_r}{\mu} [\psi(R, \theta) - \zeta_0] + \frac{S r_0^2}{4} \left[1 - R^2 + \sum_m C_m (1 - R^{4m} \cos 4m\theta) \right] \quad (4.19)$$

where $R = \frac{r}{r_0}$

If by taking r_β as the characteristic dimension we can get:

$$u(R, \theta) = \frac{E_0 \varepsilon_0 \varepsilon_r}{\mu} [\psi(R, \theta) - \zeta_0] + \frac{S r_\beta^2}{4} \left[1 - R^2 + \sum_m C_m ((-1)^m - R^{4m} \cos 4m\theta) \right] \quad (4.20)$$

where $R = \frac{r}{r_\beta}$

Formulate the boundary condition along DA as $u(R_\theta, \theta_i) = 0$, $\psi(R_\theta, \theta_i) = \zeta_0$,

$0 \leq \theta_i \leq \beta$. Substituting the boundary condition into Eq. (4.20) gives,

$$1 - R_\theta^2 + \sum_m C_m [(-1)^m - R_\theta^{4m} \cos 4m\theta_i] = 0 \quad (4.21)$$

where $0 \leq \theta_i \leq \beta$

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The boundary condition is to be satisfied at M discrete boundary points along the arc DA at the specific intervals. Then the coordinate values of $M(R_\theta, \theta_i)$ pairs along the boundary curve at arbitrarily selected M boundary points (R_θ, θ_i) , $i = 1, 2, 3 \dots M$ can be chosen. So M linear algebraic equations each containing the first M C_m can easily be generated. The solution is thus complete since all constants have been determined by satisfying the boundary conditions at M discrete boundary points. It is more convenient, therefore to divide the angle ACD of Fig 4.4(b) into M equal α and at each α , R_θ and θ_i is computed by applying the cosine law to a triangle BOC.

$$R_\theta^2 = 3 - 2\sqrt{2} \cos \alpha \quad 0 \leq \alpha \leq \frac{\pi}{4}$$

$$\theta_i = \tan^{-1} \frac{\sqrt{2} \sin \alpha}{2 - \sqrt{2} \cos \alpha} \quad (4.22)$$

where $R_\theta = \frac{r}{r_\beta}$

For a closed-end microchannel, mathematically it fulfills the volumetric flow rate of the four-point-star microchannel is equal to zero, which is shown in Eq. (4.23).

$$\iint_A u(r, \theta) r dr d\theta = 0 \quad (4.23)$$

Integrating Eq. (4.20) with respect to R and subsequently changing the integral from θ to α , the volume flow rate is obtained, and hence the pressure gradient is

$$-\frac{dP}{dz} = - \frac{\iint_A E_0 \varepsilon_0 \varepsilon_r (\psi(R, \theta) - \zeta_0) dA}{\frac{r_\beta^4}{4} \int_0^{\pi/4} R_\theta^2 \left\{ \frac{1}{2} \left[1 + \sum_{m=1}^M C_m (-1)^m \right] - \left[\frac{1}{4} R_\theta^2 + \sum_{m=1}^M C_m \frac{1}{4m+2} R_\theta^{4m} \cos 4m\theta \right] \right\} f(\alpha) d\alpha} \quad (4.24)$$

R_θ and θ_i are direct functions of α and are given by the Eq. (4.22).

$f(\alpha)$ is a conversion factor as

$$f(\alpha) = -\frac{\sqrt{2}\cos\alpha-1}{-3+2\sqrt{2}\cos\alpha} \tag{4.25}$$

Eq. (4.24) gives the induced pressure gradient in a closed-end four-point-star microchannel under the steady state dc electric field. Substituting the induced pressure gradient into Eq. (4.20) gives the steady state velocity distribution within the closed-end microchannel.

4.2.3 Electroosmotic Flow in other Shaped Microchannels

4.2.3.1 Comparison of the Semi-analytical Approach with Analytical Solution for a Closed-End Rectangular Microchannel

Figure 4.5 Cross-section of one-quarter of a rectangular microchannel

Before the semi-analytical approach is employed on microchannels with other geometrical shapes, the proposed approach is compared with the existing analytical solution (Marcos *et al.*, 2004). The electroosmotic velocity distribution in a one-quarter of a rectangular microchannel (Fig. 4.5) is given by Eq. (4.26) and the induced pressure

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gradient from Eq. (4.27) is given by:

$$u(R, \theta) = \frac{E_0 \varepsilon_0 \varepsilon_r}{\mu} [\psi(R, \theta) - \zeta_0] + \frac{S a^2}{4} \left[1 - R^2 + \sum_{m=1}^M C_m (1 - R^{2m} \cos 2m\theta) \right] \quad (4.26)$$

where $R = \frac{r}{a}$

$$-\frac{dP}{dz} = - \frac{\iint_A E_0 \varepsilon_0 \varepsilon_r (\psi(R, \theta) - \zeta_0) dA}{\frac{a^4}{4} \int_0^{\pi} R_\theta^2 \left\{ \frac{1}{2} \left[1 + \sum_{m=1}^M C_m \right] - \left[\frac{1}{4} R_\theta^2 + \sum_{m=1}^M C_m \frac{1}{2m+2} R_\theta^{2m} \cos 2m\theta \right] \right\} d\theta} \quad (4.27)$$

The parametric equations of the boundary line BAD may be expressed as

$$R_\theta = \begin{cases} \frac{1}{\cos \theta_i} & 0 \leq \theta_i \leq \tan^{-1} AR \\ \frac{AR}{\sin \theta_i} & \tan^{-1} AR < \theta_i \leq \frac{\pi}{2} \end{cases} \quad (4.28)$$

where $AR = \frac{b}{a}$, an aspect ratio.

Figure 4.6 Comparison of the semi-analytical solution (M=12) and the Green Function's solution.

b:a=0.4, $n_0=10^{-6}M$, $\zeta_0=75mV$, $E_0=10000V/m$, $K=186.09$. Analytical solution pressure

gradient=5209.60, semi-analytical solution pressure gradient=5209.02.

Fig. 4.6 shows the comparison between the Green’s Function (Marcos *et al.*, 2004) and the semi-analytical solutions for the electroosmotic flow in the closed-end rectangular microchannels. From the figure, it is clearly seen that the solutions are identical, and hence validated the semi-analytical approach.

4.2.3.2 Electroosmotic Flow in Elliptic Microchannels

Figure 4.7 Cross-Section of an ellipse

Let the major and minor semi-axes of an ellipse labeled as a and b , as shown in Fig. 4.7. The major semi-axes a have been taken as the characteristic dimension.

Instead of taking M subdivisions of the boundary curve, only the first coefficient in the series is retained and is determined at $\theta_i = \frac{\pi}{2}$, $R_\theta = \frac{b}{a}$. Hence, the electroosmotic velocity distribution in an elliptic microchannel with the only first coefficient is given as:

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$$u(R, \theta) = \frac{E_0 \epsilon_0 \epsilon_r}{\mu} [\psi(R, \theta) - \zeta_0] + \frac{Sa^2}{4} \left[1 - R^2 + \frac{b^2 - a^2}{b^2 + a^2} (1 - R^2 \cos 2\theta) \right] \quad (4.29)$$

where $R = \frac{r}{a}$

The boundary conditions $u(R_\theta, \theta_i) = 0$, $\psi(R_\theta, \theta_i) = \zeta_0$, $0 \leq \theta_i \leq \frac{\pi}{2}$ are substituted into Eq. (4.29), we get R_θ as a function of θ_i and is given as.

$$\frac{1}{R_\theta^2} = \cos^2 \theta_i + \frac{a^2}{b^2} \sin^2 \theta_i \quad (4.30)$$

For a closed-end microchannel, the induced pressure gradient is

$$-\frac{dP}{dz} = -\frac{\iint_A E_0 \epsilon_0 \epsilon_r (\psi(R, \theta) - \zeta_0) dA}{\frac{\pi a^3 b^3}{16 a^2 + b^2}} \quad (4.31)$$

If $a \rightarrow b$, Eq. (4.29) reduces to the expression for the flow in a circular cylinder.

4.2.3.3 Electroosmotic Flow in Star Point Family Microchannels

Figure 4.8 Cross-section of the star point family

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The family of star microchannels can be parameterized by a number of star points, p which corresponds to the number of curved sides (see in Fig. 4.8). The electroosmotic velocity distribution in the star point family microchannel is given by Eq. (4.32) and the pressure gradient is obtained from Eq. (4.33):

$$u(R, \theta) = \frac{E_0 \varepsilon_0 \varepsilon_r}{\mu} [\psi(R, \theta) - \zeta_0] + \frac{S r_\beta^2}{4} \left[1 - R^2 + \sum_{m=1}^M C_m ((-1)^m - R^{mp} \cos mp\theta) \right] \quad (4.32)$$

where $R = \frac{r}{r_\beta}$

$$-\frac{dP}{dz} = - \frac{\iint_A E_0 \varepsilon_0 \varepsilon_r (\psi(R, \theta) - \zeta_0) dA}{\frac{r_\beta^4}{4} \int_0^{\frac{\pi}{p}} R_\theta^2 \left\{ \frac{1}{2} \left[1 + \sum_{m=1}^M C_m \right] - \left[\frac{1}{4} R_\theta^2 + \sum_{m=1}^M C_m \frac{1}{mp+2} R_\theta^{mp} \cos mp\theta \right] \right\} d\theta} \quad (4.33)$$

The boundary is derived as

$$R_\theta^2 = \frac{1 + \frac{1}{\cos^2 \frac{\pi}{p}} - 2 \frac{\cos \alpha}{\cos \frac{\pi}{p}}}{tg^2 \frac{\pi}{p}} \quad 0 \leq \alpha \leq \frac{\pi}{2} - \frac{\pi}{p} \quad (4.34)$$

$$\theta_i = \tan^{-1} \frac{\sin \alpha}{ctg \frac{\pi}{p} - \cos \alpha}$$

where $R_\theta = \frac{r}{r_\beta}$

The semi-analytical solutions of the electroosmotic flows velocity with $p=4$ (four-point-star) are presented with a detailed description of computational procedures. The actual scheme of calculation with the foregoing equations for the family of star

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microchannels is the same as reported.

4.2.4 Results and Discussions

In all the calculations, KCl solution (valence $z_v = 1$) is used as the electrolyte. The density, ρ , viscosity, μ , and dielectric constant, ϵ_r of the electrolyte are taken to be the same as those for water. These are 1000 kg m^{-3} , $1.12 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$ and 80 respectively. The permittivity of vacuum, ϵ_0 is $8.85 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$. The temperature of the electrolyte is $T = 298.15 \text{ K}$. The strength of the electric field is $E_0 = 10000 \text{ V m}^{-1}$. The reference velocity is chosen as 1 m s^{-1} .

4.2.4.1 The Effect of the Sharp Corner on the Electric Potential and Velocity Distributions

When two interfaces are sufficiently close to each other, the electrical double layers will overlap and interact with one another. The understanding of the effects of the overlapped EDL fields is important to the study of interaction forces between colloidal particles, electrokinetic flows in fine capillaries and many other electrokinetic phenomena. The star-point-family channels have sharp corners at the star tips. Hence at the sharp corners, EDL overlapped. It would be important to know the effect of the sharp corners on the electrokinetic flow.

Due to the symmetry, the electric potential in a half domain, i.e from wall AE to the middle plane AO , is shown in Fig. 4.9. The bulk concentration of electrolyte is 10^{-6} M and the packed capillary radius, $R_0 = 20 \text{ } \mu\text{m}$. The calculated double layer thickness is

300 nm. In Fig. 4.9, the separation distances $11'$, $22'$, $33'$ are 300 nm, 1200 nm and 6000 nm, respectively.

Figure 4.9 Corner of a four-point-star microchannel

Fig. 4.10 shows the electric potential distributions for three different separation distances $11'$, $22'$ and $33'$ in the four-point-star corner. For the separation distance $11'$, the distance between the two walls AE and AE' is approximately 300 nm, which results in the overlapped EDL field. The solid line in Fig. 4.10 indicates the redistribution of the electrical potential on the overlapped EDL regions. The electric potential and the net charge density become stronger in the whole region due to the overlapped of the EDL fields. The electric body force is stronger in these regions.

At the separation distance $22'$, the distance between the two walls AE and AE' is about 1200 nm. This separation distance is approximately four times the double layer thickness. The dashed line $22'$ in Fig. 4.10 shows the change of the electric potential from the wall to the center is larger than that of the solid line $11'$, but smaller than that

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of the dotted line 33'.

For the separation distance 33', the distance between the walls is 6000 nm, which is about 20 times of the thickness of the double layer. Due to the large separation distance, the electric potential distribution exhibits the single EDL field. At the boundary wall, the values of the electric potential and the net charge density are higher and in the bulk region these values approach zero.

Figure 4.10 Comparison of the electric potential distributions for three separation distances.

Figs. 4.11 and 4.12 show the comparison of the dimensionless electric potential and velocity distributions along OD and along OA (sharp corner), respectively. Fig. 4.7 indicates that due to the overlapped EDL fields at the sharp corner, high values of the electric potential occur. This corner region ($1-A-1'$) is around 4 percent the size of the whole region ($E-A-E'$). Near the wall, the velocity profiles are influenced by viscous and electrostatic forces. Fig. 4.8 shows that the velocity remains almost zero at

the corner due to the narrow gap of the order of the EDL thickness. Thus, viscous effects and no-slip boundary condition dominate the flow field.

Figure 4.11 Comparison of the dimensionless electric potential distributions along OD and along OA (sharp corner).

Figure 4.12 Comparison of the dimensionless closed-end velocity distributions along OD and along OA (sharp corner).

4.2.4.2 Effect of the Packed Capillary Radius R_0 and Concentration on the Closed-End Velocity Distribution and Induced Pressure Gradient

Fig. 4.13 shows the velocity profiles for different values of concentration along OD. Three concentrations, $n_0 = 10^{-6}$ M, 10^{-5} M and 10^{-4} M with $\zeta_0 = 25$ mV and $R_0 = 20 \mu\text{m}$ are chosen and the corresponding K values are 35.59, 112.56 and 355.95. Table 4.1 shows the corresponding induced pressure gradient. The figure shows an abrupt velocity variations between the boundary and the center region for a strong electrolyte, as the *Debye–Hückel* parameter is proportional to the square root of the bulk ionic concentration, n_0 . The variation of the ionic concentration will alter the velocity profile at the closed-end. The velocity profile in the closed-end microchannel indicates that there exists a reverse flow in the bulk liquid region. This reverse flow is generated by the induced back pressure to counter balance the electroosmotic flow so that the net

Figure 4.13 Electroosmotic velocity distributions along OD of the closed-end four-point-star microchannel with different concentrations.

flow rate is zero. It is noted that the velocity profile at the bulk liquid region exhibits a

parabolic profile due to the induced back pressure gradient. With the increase of the ionic concentration, the back pressure gradient induced by the closed-end increases.

Table 4.1 Induced pressure gradient for different concentration $n_0(M)$

Concentration, $n_0(M)$	10^{-4}	10^{-5}	10^{-6}
Induced pressure gradient, $dP / dz(Pa / m)$	155,078.66	151,710.69	142,030.56

Fig. 4.14 shows the velocity profiles for different radii of the packed capillary, R_0 . The parameters are $\zeta_0 = 25 \text{ mV}$ and $n_0 = 10^{-5} \text{ M}$. Three radii, $R_0 = 5 \mu\text{m}$, $10 \mu\text{m}$, $15 \mu\text{m}$ are selected in the formation of the four-point-star dimensions with the corresponding values of $K = 28.14$, 56.28 and 84.42 . Table 4.2 shows the corresponding induced pressure gradient. The flow area of the microchannel depends on the radius of the packed capillary, R_0 , and it increases with increasing, R_0 .

Figure 4.14 Electroosmotic velocity distributions along OD of the closed-end four-point-star microchannel with different packed capillary radii.

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The results show that as the flow area decreases, the reverse flow velocity increases. Also the induced backpressure gradient increases rapidly with decreasing, R_0 . Hence the miniaturization of the flow channels to relatively narrow pores may have a dramatic effect on the specifications of electrokinetic actuators. It is evident that devices with highly miniaturized channels or even microscopic pores should be capable of generating extremely high pressure.

Table 4.2 Induced pressure gradient for different radii of the packed capillary, R_0

Packed capillary radius, $R_0(\mu m)$	5	10	15
Induced pressure gradient, $dP / dz (Pa / m)$	2,216,787.00	588,374.68	266,918.50

4.2.4.3 Comparison of the Induced Pressure Gradient for Different Shapes with the Same Packed Capillary Radius, R_0

Fig. 4.15 shows the comparison of the velocity profiles for three different cross-sections: three-point-star, four-point-star and circular channels at the same, R_0 . Table 4.3 shows the induced pressure gradient within the closed-end channel.

Figure 4.15 Comparison of the closed-end velocity distributions for circular, four-point-star and three-point-star with the same $R_0=20\ \mu m$ along OD.

The results show the three-point-star achieves the highest induced pressure. The induced pressure gradient of the three-point-star microchannel is forty times that of the circular and four times that of the four-point-star. Therefore, for a given R_0 , the three-point-star shape is able to generate the highest pressure gradient. For a given R_0 , the area of the three-point-star is the smallest and it induces the highest pressure gradient.

Table 4.3 Induced pressure gradient of the same R_0 for various microchannels

	$R_0\ (\mu m)$	$dP/dz(Pa/m)$	K
Circular	20.00	41,183.96	130.26
Four-point-star	20.00	426,091.68	35.59
Three-point-star	20.00	1,899,042.00	13.37

4.2.4.4 Comparison of the Induced Pressure Gradient for Different Shapes with the Same Cross Section Area

Fig. 4.16 shows comparison of the closed-end velocity distributions for circular, four-point-star and three-point-star channels with the same cross section area. Table 4.4 shows the corresponding induced pressure gradient within the closed-end channels. For the same cross section area, the induced pressure gradient of the star-family microchannels is about three-times higher than that of the circular. Also the induced pressure gradient of the four-point-star is a little higher than that of the three-point-star. Thus, for a given cross section area, the star family induces higher pressure gradient due to the effects of sharp corners.

Figure 4.16 Comparison of the closed-end velocity distributions for circular, four-point-star and three-point-star with the same cross section area along OA.

Table 4.4 Induced pressure gradient of the same cross section area
for various microchannels

	$R_0 \text{ (}\mu\text{m)}$	$dP / dz \text{ (Pa / m)}$	K
Circular	10.45	146,467.81	68.09
Four-point-star	20.00	426,091.68	35.59
Three-point-star	46.14	410,572.03	30.85

4.2.5 Electroosmotic Flow with Step Changes in Zeta Potential and Cross Section

The model can be further developed for fully developed laminar flow caused by both pressure gradient and an electric field in a long and narrow channel with step changes in zeta potential and cross section as shown in Fig. 4.17. The analysis is restricted to channels that are very long compared to their height and width. Solutions are derived for the fully developed regions away from the step changes in cross section and zeta potential. The Reynolds number in microchannels is generally in the order of unity or less. For such small Reynolds numbers, the entrance length depends on the viscous terms in the Navier–Stokes equation. Since the microchannels under consideration are long compared to their height or width, the assumptions of fully developed flow and electric fields are justified over the vast majority of the channel length.

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Figure 4.17 Rectangular channel with different cross sections and different zeta potentials.

For each region, the resulting solution for the velocity profile in the n th microchannel region is

$$u_n(R, \theta) = u_{EOF} + \left(-\frac{dP}{dz}\right)_n \times \frac{a^2}{4\mu} [1 - R_n^2 + \sum_{m=1}^M C_m (1 - R_n^{2m} \cos 2m\theta)] \quad R = \frac{r}{a} \quad (4.35)$$

Define the geometry coefficient $GC_n = \frac{a^2}{4\mu} [1 - R_n^2 + \sum_{m=1}^M C_m (1 - R_n^{2m} \cos 2m\theta)]$.

The corresponding volumetric flow rate of the n th region is

$$Q_n = \iint_A E_0 \epsilon_0 \epsilon_r (\psi(R, \theta) - \zeta_0) / \mu dA + \frac{Sa^4}{4} \int_0^{\pi/2} R_\theta^2 \left\{ \frac{1}{2} \left[1 + \sum_{m=1}^M C_m \right] - \left[\frac{1}{4} R_\theta^2 + \sum_{m=1}^M C_m \frac{1}{2m+2} R_\theta^{2m} \cos 2m\theta \right] \right\} d\theta \quad (4.36)$$

Define the geometry coefficient of the corresponding volumetric flow rate

$$QC_n = \frac{a^4}{4\mu} \int_0^{\pi/2} R_\theta^2 \left\{ \frac{1}{2} \left[1 + \sum_{m=1}^M C_m \right] - \left[\frac{1}{4} R_\theta^2 + \sum_{m=1}^M C_m \frac{1}{2m+2} R_\theta^{2m} \cos 2m\theta \right] \right\} d\theta.$$

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The volumetric flow rates in each region must be equal to satisfy continuity for an incompressible fluid,

$$Q_1 = Q_2 = \dots = Q_N = Q \quad (4.37)$$

where N is the total number of regions and Q is the volumetric flow rate through the channel.

Additionally, the overall pressure drop applied along the channel must equal the sum of the pressure drops along the individual region,

$$-L_1 \left(\frac{dP}{dz} \right)_1 - L_2 \left(\frac{dP}{dz} \right)_2 - \dots - L_N \left(\frac{dP}{dz} \right)_N = \Delta P \quad (4.38)$$

where L_N is the length of region N , $\left(\frac{dP}{dz} \right)_N$ is the pressure difference of the region N and ΔP is the pressure difference between the channel entrance and exit.

The tangential component of the electric field in region N is

$$E_n = \frac{V_n}{L_n} \quad (4.39)$$

The current, I , through each region must be the same

$$I = \frac{V_1}{R_1} = \frac{V_2}{R_2} = \dots = \frac{V_N}{R_N} = \frac{V}{R} \quad (4.40)$$

The resistance of each region is proportional to its length and inversely proportional to its cross-sectional area

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$$E_n = \frac{V}{A_n \sum_{i=1}^N (L_i / A_i)} \quad (4.41)$$

Solving Equations (4.35-4.41) for the N unknown pressure gradients

$$\left(-\frac{dP}{dz}\right)_n = \frac{\frac{1}{QC_n} \left(\frac{\varepsilon_0 \varepsilon_r V \left(\sum_{i=1}^N \frac{L_i}{QC_i} \zeta_n - \sum_{i=1}^N \frac{L_i \zeta_i}{QC_i} \right) + \Delta P}{\sum_{i=1}^N \frac{L_i}{A_i}} \right)}{\sum_{i=1}^N \frac{L_i}{QC_i}} \quad (4.42)$$

These results can be inserted into Eqs. (4.35) and (4.36) to yield the velocity profile and volumetric flow rate in each section. The velocity profile in region n reduces to

$$u_n(R, \theta) = \frac{\varepsilon_0 \varepsilon_r V (\psi_n(R, \theta) - \zeta_{n0})}{\mu A_n \sum_{i=1}^N (L_i / A_i)} + \frac{\frac{1}{QC_n} \left(\frac{\varepsilon_0 \varepsilon_r V \left(\sum_{i=1}^N \frac{L_i}{QC_i} \zeta_n - \sum_{i=1}^N \frac{L_i \zeta_i}{QC_i} \right) + \Delta P}{\sum_{i=1}^N \frac{L_i}{A_i}} \right)}{\sum_{i=1}^N \frac{L_i}{QC_i}} \times GC_n \quad (4.43)$$

and the volumetric flow rate is

$$Q_n = \frac{\varepsilon_0 \varepsilon_r}{\mu} \iint_{A_n} \frac{V (\psi_n(R, \theta) - \zeta_{n0})}{A_n \sum_{i=1}^N (L_i / A_i)} dA_n + \frac{\frac{1}{QC_n} \left(\frac{\varepsilon_0 \varepsilon_r V \left(\sum_{i=1}^N \frac{L_i}{QC_i} \zeta_n - \sum_{i=1}^N \frac{L_i \zeta_i}{QC_i} \right) + \Delta P}{\sum_{i=1}^N \frac{L_i}{A_i}} \right)}{\sum_{i=1}^N \frac{L_i}{QC_i}} \times QC_n \quad (4.44)$$

To illustrate the results of the models developed in this section, a case involving a rectangular channel with two regions is discussed in comparison with the published data (Brotherton and Davis, 2004). Using the following parameters:

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$a_1=100\ \mu m, b_1=40\ \mu m, \zeta_1=25\ mV, L_1=1\ cm$

$a_2=100\ \mu m, b_2=20\ \mu m, \zeta_2=50\ mV, L_2=1\ cm$

Figure 4.18 Velocity profile of the first channel

Figure 4.19 Velocity profile of the second channel

The velocity profile (Fig. 4.18 and Fig. 4.19) in each region of Fig. 4.17 is a superposition of a flat profile due to the electroosmotic flow and a parabola-like profile

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due to the pressure-driven flow. There is a difference of the two models at the boundary. The model presented by Brotherton and Davis (2004) neglects the existence of the electric double layer and assumes the slip boundary condition, but our proposed model uses the no-slip boundary condition.

4.2.6 Summary

In this section, a semi-analytical scheme is used to model the steady, fully developed, electroosmotic driven flow in the closed-end irregularly shaped microchannels. The induced pressure gradient has been studied under the effects of the ionic concentration, the packed capillary radius. The comparisons of the induced pressure gradient and velocity distributions for different cross-section area have been presented. It is found that the star-point-family channels have sharp corners where the EDL overlaps. This overlapped EDL results in higher values of the electric potential and net charge density. At the star corners, due to the narrow gaps of the order of EDL thickness, viscous effects and the overlapped EDL fields significantly influence the flow field. Moreover, the induced pressure gradient for a four-point-star microchannel increases with increasing the ionic concentration. While the induced pressure gradient decreases with increasing the packed capillary radius. For a given packed capillary radius, the star-point-family is able to generate the highest back pressure gradient. For the same cross section area, the star-point-family induces higher pressure gradient due to the effects of sharp corners.

4.3 Dynamics Aspects of Electroosmotic Flow

This section presents an analysis of the frequency and time dependent electroosmotic flow in open-end and closed-end microchannels of arbitrary cross-section shape. The underlying mathematical modeling and solution seem to pose more challenges than those in simple geometries. The dynamic responses of an electroosmotic flow and the pressure gradient of the closed-end under the applications of both sinusoidally alternating and constant electric fields are discussed. The flow can be modeled as a unidirectional flow through a bundle of small parallel packed capillaries of radius, R_0 as shown in Fig. 4.3.

4.3.1 Dynamics of Electroosmotic Flow

Here, we consider the fluid flow in a four-point-star microchannel as shown in Fig. 4.20. The channel wall is assumed to be uniformly charged with the zeta potential, ζ_0 . When an external time-dependent electric field, $E(t)$ is applied along the axial direction of the channel, the liquid moves along the channel as a result of the interaction between the net charge density in the EDL and the applied electric field. To analyze the flow, the coordinate axis is placed at the origin point, O. EDL forms along the arc walls and the no-slip boundary condition is applied along these arc walls.

Figure 4.20 Cross section of the four-point-star microchannel

The Navier-Stokes equation represents the fluid flow in general cases. However, it has to be modified to include the electric force generated by the interaction between the EDL and the applied electrical field. The equation of motion for an incompressible Newtonian liquid has been modified and it becomes

$$\rho \frac{\partial \vec{V}}{\partial t} + \rho (\vec{V} \cdot \nabla) \vec{V} = -\nabla \vec{P} + \vec{F} + \mu \nabla^2 \vec{V} \tag{4.45}$$

where $\vec{V}$ is the velocity vector, ρ is the density of the fluid and, μ is the dynamic viscosity of the fluid. If the gravity effect is negligible, the force $\vec{F}$ is caused only by the action of the induced electrical field on the net charge density in the EDL regions of the electrolyte. For a fully developed flow in the domain, the components of velocity $\vec{V}$ satisfy $u = u(x, y)$ and $v = w = 0$ in the Cartesian coordinates. Hence, the equation becomes

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$$\rho \frac{\partial u}{\partial t} = -\frac{dP}{dz} + \mu \nabla^2 u + E(t) \rho_e \quad (4.46)$$

where ρ_e is the local net charge density in the electrolyte due to the presence of the EDL.

Assuming the Boltzmann distribution, it is expressed as

$$\rho_e = -2z_v e n_0 \sinh\left(\frac{z_v e \psi}{k_b T}\right) \quad (4.47)$$

where n_0 and z_v are the bulk concentration and the valence of type- i ions, respectively; e is the elementary charge, k_b is the Boltzmann constant, and T is absolute temperature.

The external applied electric field can be expressed as

$$E(t) = E_0 \sin(\omega t) \quad (4.48)$$

Introducing the dimensionless parameters

$$\begin{aligned} \bar{u} &= \frac{u}{U_{ref}} & \bar{x} &= \frac{x}{D_h} & \bar{y} &= \frac{y}{D_h} & \bar{z} &= \frac{z}{D_h \text{Re}_0} \\ \bar{P} &= \frac{P}{\rho U_{ref}^2} & \bar{\omega} &= \frac{\rho D_h^2}{\mu} \omega & \bar{\psi} &= \frac{z_v e \psi}{k_b T} & \bar{t} &= \frac{\mu}{\rho D_h^2} t \\ \text{Re}_0 &= \frac{\rho U_{ref} D_h}{\mu} & \bar{E} &= \frac{E_0 D_h \text{Re}_0}{\zeta_0} & \bar{G} &= \frac{2z_v e n_0 \zeta_0}{\rho U_{ref}^2} \end{aligned} \quad (4.49)$$

The reference velocity U_{ref} is chosen as $1.0 \times 10^{-3} \text{ m/s}$. Using the above scaling relationships and substituting Eqs. (4.47) and (4.48) into Eq. (4.46), one can write the nondimensional equation as:

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$$\frac{\partial \bar{u}}{\partial \bar{t}} = \frac{\partial^2 \bar{u}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{u}}{\partial \bar{y}^2} - \frac{d\bar{P}}{d\bar{z}} - \bar{G}\bar{E} \sin(\bar{\omega}\bar{t}) \sinh \bar{\psi} \quad (4.50)$$

4.3.2 Electric Potential Distribution

It was shown by Kang *et al.* (2002) that for microchannels with fully-developed electroosmotic flows under the time-dependent electric field, the EDL electrical potential distribution can still be described by the well-known Poisson-Boltzmann equation provided that the frequency of the electric field is not very high ($< 1 \text{ MHz}$).

The Poisson-Boltzmann equation in a four-point-star domain is expressed as

$$\nabla^2 \psi = \frac{2z_v e n_0}{\varepsilon_r \varepsilon_0} \sinh \left(\frac{z_v e \psi}{k_b T} \right) \quad (4.51)$$

where ε_0 is the permittivity of vacuum and ε_r is the dielectric constant of the solution.

Defining the Debye-Hückel parameter $\kappa = \left(2z_v^2 e^2 n_0 / \varepsilon_r \varepsilon_0 k_b T \right)^{1/2}$ and the hydraulic diameter of the microchannel as $D_h = \frac{2(4-\pi)R_0}{\pi}$ and introducing the dimensionless groups $\bar{x} = x / D_h$, $\bar{y} = y / D_h$, $K = \kappa D_h$ and $\bar{\psi} = z_v e \psi / k_b T$, the above equation can be non-dimensionalized as

$$\nabla^2 \bar{\psi} = K^2 \sinh(\bar{\psi}) \quad (4.52)$$

where κ has the unit of m^{-1} and $\lambda_D = 1 / \kappa$ is referred to the characteristic thickness of the EDL.

4.3.3 Numerical Method

Generally speaking, the non-linear Poisson-Blotzmann Eq. (4.52) can not be solved analytically. Taylor series expansion is used to linearize the non-linear source term in Eq. (4.52):

$$\sinh \bar{\psi}_{n+1} = \sinh \bar{\psi}_n + (\bar{\psi}_{n+1} - \bar{\psi}_n) \cosh \bar{\psi}_n \quad (4.53)$$

As reverse flow occurs in the bulk liquid region of a closed-end microchannel due to the induced back pressure, the net flow rate is therefore zero. This is expressed as

$$Q_{EOF} + Q_{Pressure} = 0 \quad (4.54)$$

For a closed-end microchannel, the velocity profile is the linear superposition of the electroosmotic flow and the pressure gradient flow. The validity of this superposition is given by Soderman and Jonsson (1996). Hence the velocity field consists of two parts:

$$\bar{u} = \bar{u}_{EOF} + \bar{u}_{VP} \quad (4.55)$$

where $\bar{u}_{VP}$ corresponds to the pressure driven channel flow velocity (i.e. Poiseuille flow), and $\bar{u}_{EOF}$ is the electroosmotic flow velocity.

Then Eq. (4.50) can be changed to:

$$\frac{\partial \bar{u}_{EOF}}{\partial \bar{t}} = \frac{\partial^2 \bar{u}_{EOF}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{u}_{EOF}}{\partial \bar{y}^2} - \bar{G}\bar{E} \sin(\bar{\omega}\bar{t}) \sinh \bar{\psi} \quad (4.56(a))$$

$$\frac{\partial \bar{u}_{VP}}{\partial \bar{t}} = \frac{\partial^2 \bar{u}_{VP}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{u}_{VP}}{\partial \bar{y}^2} - \frac{d\bar{P}}{d\bar{z}} \quad (4.56(b))$$

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The numerical scheme used to solve the proposed mathematical models is based on the control volume method (Patankar, 1980). For the case of closed-end microchannel, there are the electroosmotic forces and the force due to the induced pressure. At each time step, we first calculate the electroosmotic flow velocity, $\bar{u}_{EOF}$. The numerical convergence criterion for the electroosmotic flow velocity is chosen $|\bar{u}_{n+1} - \bar{u}_n| / \bar{u}_n \leq 10^{-6}$ for the calculated non-dimensional potential values at each of the grid point for two successive iterations. Hence the volume flow rate Q_{EOF} is obtained. To calculate $\bar{u}_{VP}$ and $Q_{Pressure}$, Eq. 4.56(b) is solved iteratively after a first guess value for the pressure gradient. From the condition of zero total flow rate for the closed-end microchannels, it implies that $Q_{Pressure}$ is equal to Q_{EOF} . The numerical convergence criterion $|Q_{Pressure} - Q_{EOF}| \leq 10^{-8}$ is chosen. The induced pressure gradient and $\bar{u}_{VP}$ can be determined and the velocity profile of the closed-end is solved by the linear superposition, $\bar{u} = \bar{u}_{EOF} + \bar{u}_{VP}$. The source terms for the above equation are given in table 4.5. To solve the discrete algebraic equations, the line-by-line tridiagonal matrix algorithm scheme is employed. A no-slip boundary condition, $\bar{u} = 0$, and the electric potential, $\bar{\psi} = \bar{\zeta}_0$, along the boundary arc are applied.

Table 4.5 Souce terms of the EDL, dc and ac EOF of the open-end and closed-end

	Φ		S_C	S_P	
EDL	$\bar{\psi}$		$\sinh \bar{\psi}_n - \bar{\psi}_n \cosh \bar{\psi}_n$	$\cosh \bar{\psi}_n$	
Open-end	$\bar{u}$	dc	$\bar{G}\bar{E} \sinh \bar{\psi}$	0	
four-point		ac	$\bar{G}\bar{E} \sin(\bar{\omega}\bar{t}) \sinh \bar{\psi}$	0	
-star channel					
Closed-end	$\bar{u}$	dc	$\bar{u}_{EOF}$	$\bar{G}\bar{E} \sinh \bar{\psi}$	0
			$\bar{u}_{\Delta P}$	∇P	0
		ac	$\bar{u}_{EOF}$	$\bar{G}\bar{E} \sin(\bar{\omega}\bar{t}) \sinh \bar{\psi}$	0
			$\bar{u}_{\Delta P}$	∇P	0
four-point					
-star channel					

4.3.4 Comparison between the Control Volume Formulation and Analytical Solution

In the computations, KCl is used as the electrolyte solution, at a temperature of T= 298.15K, the electrolyte properties are dielectric constant $\epsilon_r = 80$, viscosity $\mu = 1.12 \times 10^{-3}$ kg/sm , and density $\rho = 999.0$ kg/m³ . The strength of the electric field is $E_0 = 10000$ V / m . The reference velocity is chosen as 1.0×10^{-3} m / s .

Figs. 4.21 and 4.22 show a comparison of the electric potential and velocity profiles between the control volume model and the analytical solution (Marcos *et al.*, 2004). The parameters used in the calculation are given below: height=100 μm ,

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width= $40\text{ }\mu\text{m}$ of a rectangular channel and $\zeta_0 = 75\text{ mV}$, concentrations of the electrolyte are $n_0 = 10^{-6}\text{ M}$ and 10^{-5} M , the corresponding K values are 186.09 and 588.49, respectively. Fig. 4.21 shows the electrical potential calculated by the control volume formulation agrees well with that from the analytical solution. The total number of the control volumes used in the computation is 40000. More volumes at the thin EDL regions are required as the electrical potential varies rapidly in these regions.

Figure 4.21 Comparison of the electric potential distribution of the closed-end rectangular microchannel between the control volume formulation and the Green’s function solution.

Figure 4.22 Comparison of the velocity distribution of the closed-end rectangular microchannel between the control volume model and the Green’s function solution.

Fig. 4.22 shows a comparison of the velocity distributions of the closed-end rectangular microchannel using the control volume model and the Green’s Function solution (Marcos *et al.*, 2004); good agreement between both methods was observed.

4.3.5 Results and Discussions

In modeling EOF in microchannels, it is important that the EDL is captured accurately. The thickness of the EDL, $\lambda_D = \left(\epsilon_r \epsilon_0 k_b T / 2 z_0^2 e^2 n_0 \right)^{1/2}$, termed as Debye length, is in the order of 10 nm-1 μ m. The region of varying potential extends to a distance of about 3 λ_D before the potential has decayed to about 2% of its value at the surface (Hunter, 1981). On the other hand, the size of microchannels utilized in many lab-on-a-chip applications are between 1 μ m and 100 μ m. As a result, K is a big number and the electroosmotic forces are concentrated within a very thin region adjacent to the surface.

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Finer meshes near these affected regions are needed to capture the EDL forces accurately. Fig. 4.23 shows that the nonuniform body fitted finer mesh is applied at the arc walls, but the size of successive control volumes away from the walls is increased in the cross section direction.

Figure 4.23 Schematic of the nonuniform body-fitted mesh

4.3.5.1 Transient Electroosmotic Flow under a dc Electric Field

4.3.5.1.1 Open-End Electroosmotic Flow under a dc Electric Field

Dimensionless transient velocity versus dimensionless distance X along OD in an open-end four-point-star channel under a dc electric field is shown in Fig. 4.24. On the application of a dc electric field, the flow begins to develop in the region adjacent to the boundary wall and the velocity increases rapidly from zero at the boundary to a maximum value within the EDL region. As time passes, the flow gradually extends to

the rest portion of the channel due to the hydrodynamic drag originated from the liquid viscosity. When the flow in the entire channel becomes steady, the flow velocity in the center channel region remains almost a constant value, resembling a plug flow. Near the wall, the velocity profiles are determined by the effects of viscous and electrostatic forces. As the distance from the wall increases, inertial and pressure forces become important and therefore the velocity field becomes dependent on time and the pressure gradient.

Figure 4.24 Dimensionless transient velocity versus dimensionless distance X along OD in an open-end four-point-star channel under a dc electric field, $K=17.80$.

4.3.5.1.2 Closed-End Electroosmotic Flow under a dc Electric Field

(a) along OD

(b) along OE

Figure 4.25 Dimensionless transient velocity versus dimensionless distance X (a) along OD (b) along OE in a closed-end four-point-star channel under a dc electric field, $K=17.80$.

Fig. 4.25 shows dimensionless transient velocity versus dimensionless distance X along OD and along OE in a closed-end four-point-star channel under a dc electric field, $K=17.80$. Due to the induced back pressure of the closed-end channel, the fluid in the center region flows in the opposite direction of the electric body forces and exhibits a parabolic flow profile. The forward and the reverse flow components in the flow profiles reveal that both forward flow and the reverse flow grow simultaneously. The intersection of the two walls (AE and AE') within the star family microchannels results in a region of overlapped EDL and thus causes an increase in the net charge density. The redistribution of the net charge density in the overlapped EDL region affects the transient electroosmotic velocity profiles. Fig. 4.25(b) shows that the velocity remains almost zero at the sharp corner region due to the narrow gap of the order of the EDL thickness; viscous effects and the no-slip boundary condition dominate the flow field.

4.3.5.2 Oscillating Electroosmotic flow under an ac Electric Field

As an alternative to traditional dc electroosmosis, numerous novel techniques have been developed to generate the flow using an ac field. A numerical approach is taken to investigate the time periodic electroosmotic flow. The governing parameter is $\bar{\omega}$, which represents the ratio of the diffusion time scale ($t_{diff} = \frac{\rho D_h^2}{\mu}$) to the period of the applied electric field ($t_E = \frac{1}{\omega}$).

4.3.5.2.1 Open-End Electroosmotic Flow under a steadily ac Electric Field

Figure 4.26 Oscillating velocity distributions versus dimensionless distance X along OD in an open-end four-point-star microchannel under ac electric field, $K=17.80$

. (a) $\bar{\omega}_1 = 4.18$ (25 kHz), (b) $\bar{\omega}_2 = 41.84$ (250 kHz).

Snapshots are presented at eight different characteristic moments:

$$\bar{\omega}t = \frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4}, \pi, \frac{5\pi}{4}, \frac{3\pi}{2}, \frac{7\pi}{4}, 2\pi.$$

Fig. 4.26 shows comparison of the characteristics of the electroosmotic flow fields under a steadily ac electric field of two different frequencies: (a) $\bar{\omega}_1 = 4.18$ (25 kHz) (b) $\bar{\omega}_2 = 41.84$ (250 kHz). Snapshots are presented at eight different characteristic

moments: $\bar{\omega}t = \frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4}, \pi, \frac{5\pi}{4}, \frac{3\pi}{2}, \frac{7\pi}{4}, 2\pi$. To illustrate the essential features of the velocity profiles we used a relatively large double layer thickness, $\lambda_D = 3 \times 10^{-6} \text{ m}^{-1}$ corresponding to a bulk ionic concentration $n_0 = 10^{-6} \text{ M}$ and $\zeta_0 = 25 \text{ mV}$. When the frequency of the electric field is low (Fig. 4.26(a)), the flow extends through the entire channel and the changes in the flow frequency follows that of the alternating electric field. As the electric field frequency increases, the perturbed flow region becomes smaller. The flow in the central channel remains almost motionless regardless of the fast oscillating flow occurring within a thin EDL region close to the channel wall.

4.3.5.2.2 Closed-End Electroosmotic Flow under a steadily ac Electric Field

Fig. 4.27 shows oscillating electroosmotic velocity distributions for two different frequencies under ac electric field in a closed-end microchannel. At a low frequency (Fig. 4.27(a)), the electroosmotic flow begins within the EDL region near the charged channel wall when electric field is applied along the channel. Because of the induced back pressure gradient in the closed-end channel, fluid at the central region flows in the reverse direction to that of the liquid in the EDL region. When the frequency of the electric field is low, the flow extends to the entire channel and the flow frequency response follows closely that of the ac electric field. As the applied frequency increases

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(Fig. 4.27(b)), the perturbed flow region becomes smaller and the flow response in the central region of the channel lags behind that of the fast

Figure 4.27 Oscillating velocity distributions versus dimensionless distance X along OD in a closed-end four-point-star microchannel under ac electric field, $K=17.80$.

(a) $\bar{\omega}_1 = 4.18$ (25 kHz), (b) $\bar{\omega}_2 = 41.84$ (250 kHz). Snapshots are presented at eight different

characteristic moments: $\bar{\omega}t = \frac{\pi}{4}, \frac{\pi}{2}, \frac{3\pi}{4}, \pi, \frac{5\pi}{4}, \frac{3\pi}{2}, \frac{7\pi}{4}, 2\pi$.

alternating applied electric field. To provide an insight into the observed scenario, we refer to the frequency-dependent Stokes penetration depth, δ_s , representing a typical length scale of the oscillatory laminar viscous flows in response to a harmonic external excitation, where δ_s is defined as (Minor,1997).

$$\delta_s = \sqrt{\frac{\mu}{2\pi\rho f}} \tag{4.57}$$

The equation shows that the penetration depth δ_s is inversely proportional to the square root of the frequency f ($\omega = 2\pi f$) of the alternating electric field.

Figure 4.28 AC closed-end EOF induced pressure gradient and applied electric field versus characteristic moments.

The induced oscillating pressure gradient is shown in Fig. 4.28. It is noted that the

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phase shift becomes larger as the frequency increases due to the effect of fluid inertia. Moreover, in contrast to the dependence of fluid velocity on frequency, a higher back pressure gradient is generated as the frequency increases. The increase of the pressure gradient with frequency is attributed to the compression of the perturbed flow region in the channel.

4.3.6 Summary

The dynamic responses of an electroosmotic flow in open-end and closed-end irregularly shaped microchannels under dc and ac applied electric fields are obtained using the control volume method. The validation of the method is confirmed by comparing it with the solution using the analytical approach for a rectangular microchannel. The numerical method developed allows similar studies to be extended to any arbitrary cross-section. The analysis shows that the flow in a closed-end channel is the superposition of the electroosmotic flow in the EDL region and the reverse pressure-driven flow in the bulk fluid region (i.e., outside the EDL region). It is shown that the ac electroosmotic flow has strong dependence on the frequency of the applied sinusoidal electric field. Moreover, it is demonstrated that the amplitude of the induced back pressure gradient increases with increasing the frequency of the electric field.

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Conclusions and future work

5.1 Concluding Remarks

The major contributions made during the course of this thesis can be summarized as following:

1. Numerical simulation of electroosmotic mixing in Y-shaped micromixers

Comprehensive mathematical model describing the electrokinetic flow mixing with complex geometries in microfluidic systems were formulated. The models developed in this study include the Laplace equation for the externally applied electric potential, modified Navier-Stokes equation for the motion of liquid driven by electrokinetic body forces and species transport equation for the concentration distribution. A SIMPLER-type algorithm calculation procedure together with a staggered grid arrangement in a boundary-fitted coordinate system was employed in the study. Based on the body fitted coordinate system, Multi-Block algorithm is implemented to simulate the complex geometry. Numerical comparisons and experimental validations for the T-shaped micromixer were conducted. Reasonably good agreement was obtained. The effects of the inlet bifurcation angle, electric field and microchannel size on the mixing efficiency of Y-shaped micromixer were investigated through the 2D body fitted, multi-block numerical simulations. The simulation results demonstrate that by altering the bifurcation angles between the inlet channels does not affect the mixing efficiency.

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2. Electrokinetic instability in micromixing

Linear stability analysis and numerical simulation model are developed to quantitatively describe the electrokinetic instability in micromixing. The models developed include the modified Navier-Stokes equation for the motion of liquid driven by electrokinetic body forces, conservation of electrical charge equation and species transport equation for the concentration distribution.

Using the linear stability analysis, the instability mechanism is explored through parametric study. The model demonstrates that a non-uniform base state of electroosmotic flow or a larger value of diffusion coefficient tends to stabilize the flow. The magnitude of zeta potential influences the growth rate of the disturbances and growth rate decreases with the increase of zeta potential. The critical electric field strength of the electrokinetic instability exhibits a strong dependence at low concentration ratios but a weaker dependence at high concentration ratios. From the conservation equation of charge, the model shows that the diffusion current term is negligible compared to the conduction current term.

Through linear stability analysis, we show that electrokinetic instability produces periodic sinusoidal concentration waves along the downstream. This perturbed concentration field affects the electric field distributions. As a result, additional positive and negative charges are induced periodically by the perturbed electric field. These induced electrical charges interact with the external applied electric field generate an

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electric body force and produce a rotating cellular flow motion. The rotating cellular flow further alternates the concentration field and leads to the growth and propagation of instability waves.

3. A novel concept on electrokinetic actuator

A novel concept on electrokinetic actuator is developed in this thesis. The electrokinetic actuator consists of three main components: an electroosmotic component, a hydraulic component and an actuator component. In the electroosmotic component, we propose the use of frequency-dependent excitation electric field over non-conductive closed-end capillaries. Since the capillaries are sealed, there will be no net flow, and hence a back pressure will be built up. This back pressure can be converted to force for actuation. For practical applications, if a high force is required, hundreds or thousands of microcapillaries can be bundled together to provide large cross sectional area and hence a large force will be produced. The electroosmotic component can be designed in various ways, such as rectangular-microchannels-packed-tube bundle or circular-microchannels-packed-tube bundle.

4. Steady state electroosmotic flow in irregularly shaped microchannels

A FEM numerical scheme is used to solve the Poisson-Boltzmann equation for study of the electroosmotic flow in irregularly shaped microchannels. Solutions of the semi-analytical approach are employed to model the steady, fully-developed electroosmotic flow in open-end and closed-end irregularly shaped microchannels. The results by this method are shown to be accurate with less computation.

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The star-point-family microchannels have sharp corners at the star tips, and there exists the overlapped EDL regions. This overlapped EDL results in higher values of the electric potential and net charge density. The redistribution of the net charge density in the overlapped EDL region affects the transient electroosmotic velocity profiles. However, at the sharp corners due to the narrow gaps, viscous effects and no-slip boundary conditions dominate the flow field. For a given packed capillary radius, R_0 , the star-point-family is able to generate the highest back pressure gradient. In addition, for the same cross sectional area, the star-point-family induces higher pressure gradient due to the effects of the sharp corners effect.

The model has been extended for fully developed electroosmotic flow caused by both pressure and electric fields in a long and narrow channel with step changes in zeta potential and cross section. The results indicate that a step cross section change causes a significant variation in the velocity profile and in the pressure distribution.

5. Dynamics Aspects of Electroosmotic Flow

The dynamic responses of an electroosmotic flow in open-end and closed-end irregularly shaped microchannels under dc and ac applied electric fields are presented using the control volume method. The validation of the method is confirmed by comparison with the analytical solution of a rectangular microchannel.

The oscillating electroosmotic flow is found to be strongly dependent on the frequency of

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the applied sinusoidal electric field. The results demonstrate that the higher frequency leads to the compression of the perturbed flow region. The induced pressure gradient increases with increasing the frequency of the applied electric field. The numerical model developed allows similar studies to be extended to any arbitrary cross-section.

5.2 Recommendations for Future Studies

Based on the results presented in this study, some recommendations are made as following for future research in order to achieve a better and more complete understanding of the electrokinetic transport phenomena in microfluidic systems.

1. Electrokinetic instability phenomenon can enhance the micromixing. However, when the electric field is very large, there exists the Joule heating phenomenon. Thus, the model in the thesis can be extended to incorporate temperature and permittivity gradients arising from the Joule heating.
2. The pressure generation ability of electroosmotic flow in a closed-end channel is very useful in many applications. It has provoked many thoughts on how to design a channel that can produce a higher force. It is suggested that future studies can be made to examine the flow in microchannels of varying cross-section area, which can either be a nozzle like microchannel or a T-shaped microchannel shown in Fig. 5.1. The purpose is to investigate the pressure distribution and possible vortices generation in the flow.

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Figure 5.1 Geometry of a T-shaped microchannel

3. The novel concept of the electroosmotic actuator has been developed. The back pressure of the microchannel has been obtained from the numerical simulation for different cross section microchannels. So the fabrication of an experimental setup to tap and measure the pressure generated by a closed-end electroosmotic system is needed.

Publications arising from this thesis

- [1] **Yali Zhang**, Teck Neng Wong, Chun Yang and Kim Tiow Ooi, “Dynamic Aspects of Electroosmotic Flow”, *Microfluidics and Nanofluidics*, 2, 205-214, 2006.
- [2] **Yali Zhang**, Teck Neng Wong, Chun Yang and Kim Tiow Ooi, “Electroosmotic Flow in Irregular Shape Microchannels”, *International Journal of Engineering Science*, 43, 1450-1463, 2005.
- [3] **Yali Zhang**, Teck Neng Wong, Kiong Chee Chai, Chun Yang and Kim Tiow Ooi, “Numerical Simulation of Electroosmotic Mixing in Y-shaped Micromixers”, In preparation.
- [4] **Yali Zhang**, Teck Neng Wong, Kiong Chee Chai, Chun Yang and Kim Tiow Ooi, “Numerical Study of the Electrokinetic Instability for the Enhancement of Micromixing”, In preparation.

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